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SOIL SCIENCE

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INFLUENCE OF SOIL ACIDITY UPON THE DECOMPOSITION OF ORGANIC MATTER IN SOILS[1]

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Pennsylvania Agricultural Experiment Station

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Soil investigations concerning factors which influence the rate of decay of organic materials have been confined primarily to studies of the stimulating effects of various soluble salts with special reference to available nitrogen and phosphorus.

Waksman and Heukelekian (3) state that there is no correlation between soil reaction and its cellulose decomposing capacity. Their conclusions are followed by the statement that fungi which take a very active part in the decomposition of cellulose in the soil will thrive readily even under the most acid conditions in which cultivated plants will barely grow at all. The authors state that similar results were obtained by Christensen, Carpentier, and Barthel and Bengtsson. In a second article dealing with carbon dioxide evolution, Waksman and Starkey (4) conclude that the addition of lime to an acid soil makes conditions more favorable for the activities of microörganisms, thus resulting in an increase in the number of bacteria (decrease of fungi) and an increase in the respiratory power of the soil.

Stoklasa and Doerell (2) found that 1 kgm. of soil of pH 7.2 produced in 24 hours 85 mgm. of carbon dioxide compared with 5 mgm. produced by a soil of pH 4.0. In their discussion of these and similar data, the authors point out the fact that soils which vary between pH 4.7 and 4.0 are frequently noticably rich in decomposable organic substances but that the acidity is so great that the bacteria can not properly develop.

It is a well-known fact that the rate of decay of organic materials in the soil is dependent upon the nature, number, and activity of soil microörganisms. The decomposition of both the residual organic matter (respiratory capacity) and applied organic materials (organic matter decomposing power) should be affected, therefore, by any soil addition or treatment that may influence the biological properties of the soil. The studies of Waksman and Heukelekian (3) on certain limed and unlimed field plot soils, show that the addition of available nitrogen, which had little influence on soil reaction, increased the unlimed soils to a cellulose decomposing capacity comparable with that of the limed soils. There are, however, no published data dealing with such studies based on a wide range in soil reaction in which the studies were undertaken primarily to determine the influence of soil acidity upon the organic matter decomposing power of soils.

METHODS

The terms "respiratory capacity" and "organic matter decomposing power of soils" as used in this text are in accordance with the definitions proposed by Waksman and Starkey (4). The former term relates to the decay of residual soil organic matter, and the latter, to the decay of applied organic materials.

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[1] Publication authorized by the director of the Pennsylvania Agricultural Experiment Station May 18, 1933 as Technical Paper No. 591. Contribution from the department of agronomy.

[2] Professor and assistant professors of soil technology respectively.

The influence of soil acidity upon the decomposition of organic matter is expressed on the basis of 250 gm. of dry soil. The soils of different pH values were treated with the several organic materials followed by a 2-week incubation period at room temperature. Water was added in amounts equivalent to 55 per cent of the water-holding capacity. The soils, placed in a series of 1-liter side-neck filter flasks, were kept in a dark cupboard during the incubation period. At 2-day intervals the accumulated carbon dioxide was measured by absorption in a train of soda-lime tubes arranged in the usual way. Seven flasks, arranged in series, were aspirated for 40 minutes, during which time 4 liters of CO_2-free air were drawn through the apparatus. The respiratory capacity of the untreated soils and the organic matter decomposing power of the treated soils were thus measured in terms of the weight of carbon dioxide produced by each 250 gm. of soil.

ORGANIC MATERIALS USED

Four organic materials were included in the study; namely, manure, cellulose (ground filter paper), cotton seed meal, and corn starch. The materials were applied at the rate of 0.5 per cent with the exception of manure, which was used at the rate of 1.0 per cent. The manure obtained from the Institute of Animal Nutrition, represented a sample of steer dung free from urine and litter.

The nitrogen as nitrate of soda was applied at a uniform rate equivalent to 42 mgm. of nitrogen. Dipotassium phosphate (K_2HPO_4) was applied at the rate of 50 mgm. Hydrated lime was applied as follows: soil Nos. 1 and 2 received no lime; No. 3, 0.172 per cent; No. 4, 0.272 per cent; No. 5, 0.319 per cent; and No. 6, 0.360 per cent.

The lime was applied to the air-dried acid soils, which were made up to optimum moisture content and incubated for 1 month. The alkaline and neutral soils, numbers 1 and 2, were incubated for the same period but received no lime. At the end of 1 month, the six soils were air-dried and treated with cellulose and nitrogen as indicated.

SOIL

The use of field soils of unknown history for such studies, selected on the basis of differences in pH range does not represent a true measure of the influence of soil reaction on the rate of decay of organic materials. As the result of differences in previous field treatments, such soils may differ widely in composition and properties other than that of soil acidity. In order, therefore, to obviate these possible variables, soils were used which had been previously prepared in the following manner. A stock soil made up of 5 parts by weight of Hagerstown silt loam from a permanent sod, 1 part air-dried sewage sludge, and 1 part of fine sand was divided into 10 equal parts of 260 pounds. Nine portions of this stock soil were treated with different amounts of sulfur. The nine sulfur-treated soils and also one portion untreated with sulfur, were arranged in a series of small field plots, 3 feet by 1.5 feet by 1 foot deep. Each

of the 10 plots were bounded by boards of appropriate width. At the end of 2 years, during which time the plots were left undisturbed (except for the removal of occasional small samples), representative samples were taken from each of the 10 plots, air dried, and passed through a 6-mesh screen. From these 10 samples, 6 which showed a maximum pH range between 7.4 and 3.2 were selected for study.

The six soils thus prepared, including also a sample of the original stock soil, were analyzed to include the following determinations—pH, total nitrogen, nitric nitrogen, organic carbon, available phosphorus (Truog Method), water-soluble inorganic salts, and water-soluble organic matter. The relative nitrifying capacity of the six plot soils and also the number of microörganisms per gram of soil were determined. The sewage sludge used contained

TABLE 1

Nature of soils used in respiration studies

SOIL NUMBER	REACTION	SULFUR APPLIED (1930)	TOTAL N	ORGANIC C	NITRIC N	AVAILABLE P†	WATER-SOLUBLE INORGANIC SALTS‡	WATER-SOLUBLE ORGANIC MATTER
	pH	*per cent*			*mgm. per 250 gm. soil*			
Stock soil*	6.3	.....	0.322	3.45	1.0	26.0	192.5	257.5
1	7.4	.....	0.171	2.08	1.5	18.5	95.0	25.0
2	7.1	0.025	0.162	1.96	1.8	23.0	93.8	22.5
3	6.0	0.075	0.165	1.98	1.0	12.8	121.2	43.8
4	4.5	0.200	0.165	2.01	1.8	13.3	418.7	41.2
5	3.8	0.350	0.159	1.85	1.8	9.0	583.8	36.2
6	3.2	0.600	0.164	1.95	3.5	7.5	822.5	56.3

* Stock soil made up of 5 parts Hagerstown silt loam, 1 part sewage sludge and 1 part sand (by weight).

† Truog method.

‡ The excess of inorganic salts in soils 3 to 6 consists largely of calcium sulfate.

the equivalent of 3.47 per cent calcium carbonate, 3.4 per cent nitrogen, 1.28 per cent phosphoric acid (P_2O_5), 17.3 per cent organic carbon, and an appreciable amount of water-soluble potash.

EFFECT OF SULFUR ON THE COMPOSITION OF THE SIX PLOT SOILS

Table 1 shows the amounts of sulfur applied to the field plots and the composition of the soils at the end of 2 years. During the 2-year period the soils lost, on an average, 49 per cent of the original nitrogen and 42 per cent of the carbon. As a result of these proportionate losses, the nitrogen-carbon ratio changed from 10.7 to approximately that of the original Hagerstown soil (12.8). During this period of organic matter decomposition the basic ash constituents of the compost were deposited in the soils, which accounts for the increased alkalinity of the first two soils of the series. There were two major factors in operation during the process of organic matter decay, each tending to

effect a change in soil reaction—the deposition of basic ash constituents of the compost and the oxidation of sulfur. The final reactions as measured by pH are shown in table 1. The abnormal acidity of soil number 6 is due to the presence of small amounts of free mineral acid. After the soil was leached with distilled water the pH approached that of soil number 5. The excess of water-soluble inorganic salts, and water-soluble inorganic salts present in the more acid soils is due to an accumulation of calcium sulfate made possible by reduced rainfall preceding the removal of the soil samples. The organic matter content of the six soils as measured by the total nitrogen and organic carbon remained fairly constant. The water-soluble organic matter, however, shows a greater accumulation in case of the more acid soils.

It becomes obvious that the changes in the nature of the six soils as determined at the end of 2 years may be attributed directly to the influence of soil acidity induced by the oxidation of the applied sulfur. These changes, as will be shown later, greatly influenced the biological properties of the several soils to which sulfur was applied. The wide differences to be noted, therefore, in the respiratory capacity and organic matter decomposing power of the six soils may be attributed to the controlling influence of soil acidity on the nature, number, and activities of the soil microörganisms.

In the interpretation of the experimental data presented in the succeeding tables, it is recognized that carbon dioxide is only one of several by-products of organic matter decay and that the fungi assimilate carbon derived from the decomposition of organic residues in a different proportion from that of bacteria. However, the assimilated carbon utilized in the synthesis of the microbial cells is eventually attacked by a new generation of microörganisms, resulting in the liberation of the carbon as carbon dioxide. There is available, in any event, sufficient experimental evidence to warrant the measurement of organic matter decay in terms of soil respiration or carbon dioxide evolution.

EXPERIMENTAL ERROR OF METHOD USED IN THE DETERMINATION OF THE RESPIRATORY CAPACITY AND ORGANIC MATTER DECOMPOSING POWER OF THE SIX SOILS OF DIFFERENT pH

Statistical studies were made on the variations in duplicate determinations of carbon dioxide recovered from similarly treated soils. Based on the total carbon dioxide recovered in 14 days involving 54 determinations in duplicate, the probable error of a single determination was found to be ± 1.95 per cent. A study of 378 duplicate determinations based on the carbon dioxide recovered at 2-day intervals gave a probable error of a single determination of ± 5.2 per cent.

The probable error involved in the procedure used as measured in terms of carbon dioxide recovered, includes, no doubt, the accumulative errors involved in the removal and weighing of duplicate samples, mixing of materials, addition of water, and manner of transferring wet soil to flasks as well as the absorption and weighing of the carbon dioxide. The higher error based on the 2-day

intervals may be expected so far as the errors due to the measurements of carbon dioxide are concerned, since the total carbon dioxide produced in 14 days represents the accumulative plus and minus differences for each 2-day period. The probable errors, however, are small as compared to the wide differences in carbon dioxide production of the six soils. The probable error data will serve as a means of determining the significance of the difference in behavior of the six soils with respect to the evolution of carbon dioxide.

RESULTS

The total carbon dioxide produced by the six soils of different pH values in relation to the various treatments is shown in table 2. These data serve to emphasize the fact that soil reaction, under the condition of this experiment, plays an important rôle in the control of the biological activities of the six soils. This is especially true in regard to the respiratory capacity of the soils. The

TABLE 2

Production of carbon dioxide in relation to the various soil treatments

SOIL NUMBER	REACTION OF SOILS	EVOLUTION OF CO_2 IN 14 DAYS									
		Soil alone	Soil + N	Soil + cellulose	Soil + cellulose + N	Soil + cellulose + N + K_2HPO_4	Soil + manure	Soil + manure + N	Soil + cottonseed meal	Soil + cottonseed meal + N	Soil + starch
	pH	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	7.4	335	411	957	1,219	1,196	856	879	1,326	1,429	1,148
2	7.1	269	324	873	1,144	1,160	857	807	1,223	1,364	1,039
3	6.0	262	370	790	1,171	1,151	774	801	1,141	1,315	1,138
4	4.5	191	322	625	797	747	555	694	1,137	1,230	1,140
5	3.8	105	164	514	733	745	353	436	954	952	1,058
6	3.2	112	155	450	488	550	267	309	888	940	1,043

two most acid soils show a value about one third that of the soil of pH 7.4. With the one exception of the starch treatment the production of carbon dioxide of the soils below pH 6.0 is considerably reduced. Apparently the most acid soils have a capacity for the decomposition of starch equal to that of the alkaline soils. The addition of soluble nitrogen failed to restore the acid soils to normal carbon dioxide production. Nitrogen stimulated the decay of the organic materials in each soil in about equal proportions and thus failed to change the relationship with respect to the relative carbon dioxide production of each soil. The addition of dipotassium phosphate to the cellulose-nitrogen treatment failed to increase the production of carbon dioxide except in case of the two most acid soils. This slight difference in the effect of the treatment caused little change in the relationship of the six soils.

The organic matter decomposing power of the six soils is shown in tables 3 and 4. The data included in these two tables are computed from the total milligrams of carbon dioxide included in table 2. The cellulose and manure

data are quite similar. In each case the decomposing power of the two alkaline soils is considerably greater than that of the acid soils. The power of the alkaline soils to decompose cotton seed meal is also much greater. The acid soils however have a greater power to bring about the decomposition of starch. The addition of soluble nitrogen had little effect in increasing the relative

TABLE 3

Organic matter decomposing power of the six soils

SOIL NUMBER	REACTION OF SOILS	*EVOLUTION OF CO_2 IN 14 DAYS						
		No nitrogen added				Addition of 42 mgm. soluble nitrogen		
		Cellulose	Manure	Cotton-seed meal	Corn starch	Cellulose	Manure	Cotton-seed meal
	pH	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	7.4	622	521	991	813	808	468	1,018
2	7.1	604	588	954	770	820	483	1,040
3	6.0	528	512	879	876	801	431	945
4	4.5	434	364	946	949	475	372	908
5	3.8	399	248	849	953	569	272	788
6	3.2	338	155	776	931	333	154	785

* Excess of that produced by soils without organic additions.

TABLE 4

Relative respiratory capacity and organic matter decomposing power of the six soils

SOIL NUMBER	REACTION OF SOILS	BASED ON EVOLUTION OF CO_2 IN 14 DAYS								
		Results expressed in terms of soil No. 1 taken as 100								
		No nitrogen added					Addition of 42 mgm. soluble nitrogen			
		Soil	Cellulose	Manure	Cotton-seed meal	Corn starch	Soil	Cellulose	Manure	Cotton-seed meal
	pH									
1	7.4	100	100	100	100	100	100	100	100	100
2	7.1	80	97	113	96	95	79	101	103	102
3	6.0	78	85	98	89	108	90	99	90	92
4	4.5	57	70	70	95	117	78	59	79	89
5	3.8	31	64	48	86	117	40	70	58	77
6	3.2	33	54	30	78	114	38	41	33	77

organic matter decomposing power of the acid soils. The data included in table 4 in which the results are expressed in terms of soil number 1 taken as 100 (percentage relations) show conclusively that the respiratory capacity and organic matter decomposing power of the six soils (excluding the starch treatment) are parallel to the reaction of the soils. In terms of the probable error, the soils of pH below 6.0 show a significant decrease in both the respiratory capacity and the organic matter decomposing power as compared with the

soils of pH 7.4 and 7.1. The results are so conclusive that it seems unnecessary to discuss further these data.

Effect of lime

In order to determine the effect of lime as a means of restoring the acid soils to normal biological activity, the four acid soils were treated with lime in amounts shown in table 5. The four limed soils together with those not limed were made up to optimum moisture content and incubated for 30 days. The soils were then air dried, treated with cellulose and cellulose-nitrogen and incubated for 2 weeks, during which time the carbon dioxide was recovered at 2-day periods in the manner already described.

The soils were treated with lime prior to the 14-day incubation in order to allow time for the soils to reach a state of equilibrium following the chemical and biological changes induced by the effect of lime. The data in table 5 show

TABLE 5

Influence of lime upon the carbon dioxide production of the four acid soils treated with cellulose

SOIL NUMBER	$Ca(OH)_2$ APPLIED*	REACTIONS OF SOILS		EVOLUTION OF CO_2 IN 14 DAYS	
		Before liming	After liming	Soil + cellulose + $Ca(OH)_2$	Soil + cellulose + $Ca(OH)_2$ + N
	per cent	*pH*	*pH*	*mgm.*	*mgm.*
1	.....	7.4	7.0	804	669
2	.....	7.1	6.6	660	717
3	0.172	6.0	7.2	692	724
4	0.272	4.5	6.8	709	710
5	0.319	3.8	6.7	749	748
6	0.360	3.2	6.3	821	712

* Soils 1 and 2 received no lime.

that the lime and nitrogen treatment restored the acid soils to normal biological activity. The failure of nitrogen to cause an increased production of carbon dioxide in case of several of the soils may be due to the fact that during the 30-day incubation period sufficient nitrates were formed to meet the soils' need. Unfortunately insufficient lime was applied to bring the three most acid soils to the same pH as that of soil number 1. The data seem to show that lime is the major limiting factor and that nitrogen is also of importance as a controlling factor in the acid soils. Figure 1 shows the relative production of carbon dioxide from the limed and unlimed cellulose treated soils.

Influence of length of incubation period on the relationship of the six soils with respect to carbon dioxide production

The results included in tables 2, 3, 4, and 5 relate to the total carbon dioxide produced at three periods of incubation in relation to several different treatments and shows that the relationship of the six soils with respect to the three

periods is approximately the same. These data therefore point to the fact that a short period of incubation as a means of establishing the relative respiratory

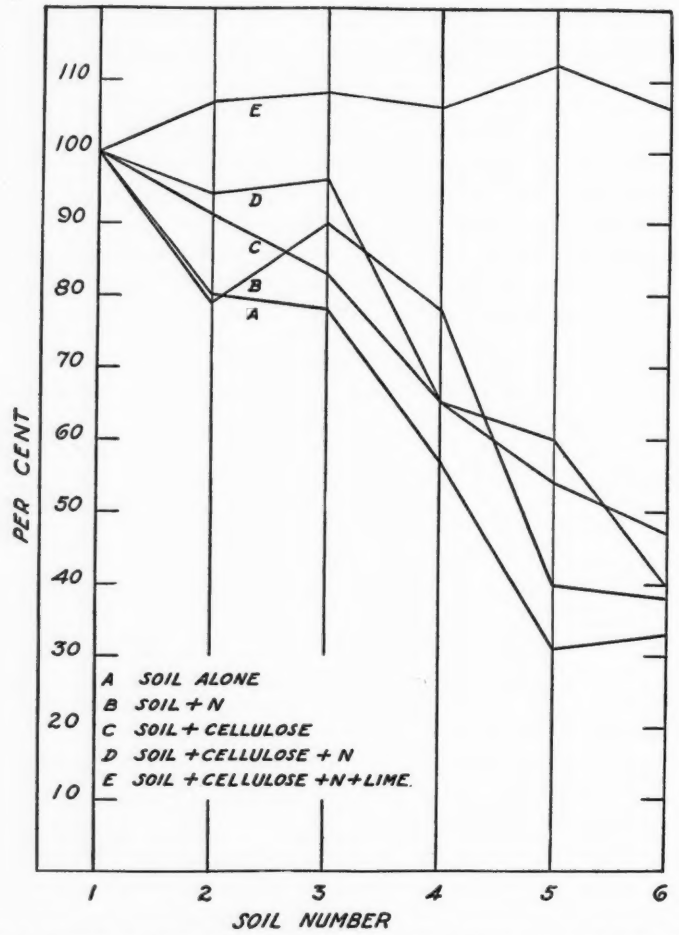

FIG. 1. COURSE OF CARBON DIOXIDE PRODUCTION IN 14 DAYS FROM THE SIX SOILS AS THE RESULTS OF DIFFERENT TREATMENTS

Data computed in terms of soil number 1 of each series taken as 100. The effect of lime in restoring the biological activities of the acid soils (numbers 3, 4, 5, 6) is shown from a comparison of series D and E.

capacity and organic matter decomposing power of several soils is comparable with that of a longer period. It is believed, however, that to measure the effect of a treatment such as lime, which brings about pronounced chemical and

biological soil changes, can not be accurately determined within a short period of incubation. The value of lime in restoring the biological activity of the four

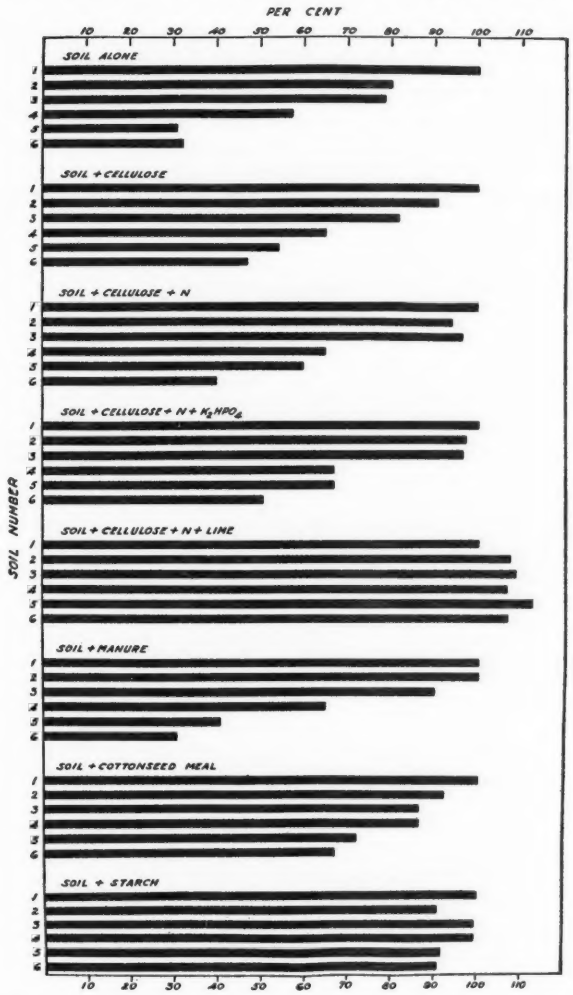
PER CENT
10 20 30 40 50 60 70 80 90 100 110
SOIL ALONE
SOIL + CELLULOSE
SOIL + CELLULOSE + N
SOIL + CELLULOSE + N + K_2HPO_4
SOIL + CELLULOSE + N + LIME
SOIL + MANURE
SOIL + COTTONSEED MEAL
SOIL + STARCH
SOIL NUMBER
1 2 3 4 5 6

FIG. 2. RELATIVE CARBON DIOXIDE PRODUCING CAPACITY OF THE SIX SOILS AS INFLUENCED BY VARIOUS TREATMENTS

Results based on the total carbon dioxide produced in 14 days in terms of soil number 1 of each series taken as 100.

acid soils is clearly shown by comparison of the data involving the soil + cellulose + nitrogen treatment with the same treatment including the addition

of hydrated lime. Figure 2 shows the relative production of carbon dioxide in relation to eight representative soil treatments.

Respiratory capacity and cellulose decomposing power of the six soils based on the fresh screened soil not air dried

It is a well-inown fact that the process of air drying soils stimulates the activities of microörganisms as the result of an increased supply of soluble salts and

TABLE 6

Influence of length of incubation period on the relative production of carbon dioxide by the six soils

SOIL NUMBER	RESULTS EXPRESSED IN TERMS OF SOIL NO. 1 TAKEN AS 100														
	Based on the total CO_2 produced in 2, 8, and 14 days														
	Soil alone			Soil + N			Soil + cellulose			Soil + cellulose + N			Soil + cellulose + N + $Ca(OH)_2$		
	Days			Days			Days			Days			Days		
	2	8	14	2	8	14	2	8	14	2	8	14	2	8	14
1	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
2	79	79	80	77	77	79	90	91	91	82	88	94	102	103	107
3	78	78	78	85	91	90	80	81	83	87	93	96	98	93	108
4	58	57	57	63	75	78	63	66	65	58	63	65	104	99	106
5	30	30	31	27	36	40	31	48	54	30	55	60	100	119	112
6	24	29	33	26	33	38	27	33	47	26	34	40	120	113	106

TABLE 7

*Respiratory capacity and cellulose decomposing power of the fresh screened soil—not air dried**

SOIL NUMBER	REACTION OF SOILS	EVOLUTION OF CO_2 IN 14 DAYS					
		In soil + cellulose	In soil alone	Due to the addition of cellulose	In soil + N + cellulose	In soil + N	Due to the addition of cellulose
	pH	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	7.3	533	213	320	879	107	772
2	7.0	427	168	259	797	98	699
3	6.4	356	162	194	804	95	709
4	5.2	272	113	159	669	97	572
5	4.4	325	72	253	378	70	308
6	3.9	198	74	124	341	83	258

* Based on the equivalent of 250 gm. dry soil.

available organic matter. It was thought that these factors might in part contribute to the marked differences established in regard to the behavior of the six soils. Fresh soils from the same plots were obtained 6 months after the removal of the first samples. The data included in table 7 are based on the results of study of these samples of fresh soils not submitted to the process of

air drying. These results are comparable with those of the air-dried soils and lead to the conclusion that the respiratory capacity and cellulose decomposing power of the acid soils are significantly different from those of pH 7.0 to 7.3 and therefore that soil acidity has a definite controlling influence on the biological activities of the soil as measured in terms of carbon dioxide production.

Number of microörganisms in the six soils and the relative nitrifying capacity

The number of microörganisms present in the limed and unlimed air-dried soils and in the fresh screened soil was determined in accordance with the procedure proposed by Fred and Waksman (1). These data, included in table 8, are based on the count at the end of 7 days of plate incubation. There is a fairly close correlation between the numbers of microörganisms, the respiratory capacity, and the organic matter decomposing power of the different soils. The effect of air drying the soils upon the stimulation of the number of micro-

TABLE 8

*Number of microörganisms and relative nitrifying capacity of the six soils**

SOIL NUMBER	RELATIVE† NITRIFYING CAPACITY (AIR-DRIED SOIL)	FRESH SCREENED SOIL NOT AIR-DRIED		AIR-DRIED SOIL			
				Unlimed		Limed	
		Bacteria	Fungi	Bacteria	Fungi	Bacteria	Fungi
		thousands	*thousands*	*thousands*	*thousands*	*thousands*	*thousands*
1	100	21,850	75	85,300	71	81,600	74.5
2	81	14,900	45	72,050	98	73,650	94
3	72	12,300	80	66,350	100	68,000	24.5
4	31	7,800	355	38,100	137	68,100	48
5	7	1,500	405	15,000	35	63,600	131
6	10	850	190	2,650	74.5	116,000	103.6

* Per gram of soil—7-day incubation.

† Based on soil 1–100.

organisms is parallel to the influence of this factor upon the rate of decay of organic matter. The effect of lime in bringing about a change in both the total number of microörganisms of the four acid soils and the proportions of bacteria and fungi are in accordance with results of various microbiologists. These data together with those shown in the preceding tables substantiate the observations of Stoklasa (2) to the effect that the accumulation of organic matter in acid soils is due to the controlling influence of acidity upon the activity of soil microörganisms. The restoration of the acid soils to normal respiratory capacity and cellulose decomposing power through the use of lime has been shown to have been made possible by a pronounced stimulation of the number of microörganisms.

The effect of acidity upon the relative nitrifying capacity of the six soils is parallel to the rate of carbon dioxide production. These data show that available nitrogen is an important factor in determining the rate of decomposition of organic materials in acid soils. It has been shown, however, that the

applications of available nitrogen, phosphorus, and potassium failed to restore the acid soils to a normal activity in relation to the two alkaline soils.

Cellulose decomposing power of limed and unlimed plot soils of the old fertilizer series

Further confirmation of the data, which show that the cellulose decomposing power of soils is influenced by soil reaction and the use of lime, is given in table 9. These data show that there is a marked difference between the cellulose decomposing power of the plot soils of tier 1 and those of tier 4, treated the

TABLE 9

Relative cellulose decomposing power of certain field plot soils of the old fertilizer series as influenced by lime

PLOT NUMBER	FIELD TREATMENT	REACTION OF SOILS		BASED ON THE MGM. CO_2 PRODUCED BY SOIL + CELLULOSE IN EXCESS OF THE SOIL ALONE	
				Soils of Tier 1 taken as 100	
		Tier 1	Tier 4	Tier 1 unlimed	Tier 4 limed
		pH	*pH*		
1	No treatment	5.8	7.3	100	159
9	PK + 24N (DB)	5.2	6.4	100	155
10	PK + 48N (DB)	5.1	6.1	100	139
11	PK + 72N (DB)	5.2	6.7	100	148
17	PK + 24N (DB)	5.0	6.7	100	132
19	PK + 48N (DB)	5.0	6.9	100	155
21	PK + 72N (DB)	5.1	6.6	100	127
26	PK + 24N ($NaNO_3$)	5.3	6.5	100	145
27	PK + 48N ($NaNO_3$)	5.4	6.4	100	125
28	PK + 72N ($NaNO_3$)	5.5	6.4	100	140
29	PK	5.2	6.3	100	154
30	PK + 24N (NH_4SO_4)	4.8	6.3	100	164
31	PK + 48N (NH_4SO_4)	4.4	5.8	100	121

same for half a century except that the plots of tier 4 received a dressing of limestone in 1923 while the plots of tier 1 have never been limed. Limestone was applied to the plot soils of tier 4 in amounts sufficient to correct the acidity in terms of the lime requirement method of the senior author (5). The data of table 9 are expressed for convenience of study in terms of the cellulose decomposing power of each plot of tier 1 taken as 100 and are based on the total carbon dioxide produced in 14 days from 250 gm. of soil. The cellulose decomposing power is measured in terms of the carbon dioxide produced by the soil + cellulose in excess of that derived from the soil alone. A study of these data shows that the limed soils in the case of each treatment have a cellulose decomposing power greatly in excess of the unlimed soils of tier 1. A

summary of the data of table 9 based on the actual milligrams of carbon dioxide produced is as follows:

	Tier 1	*Tier 4*
Average mgm. CO_2	798	1,130
Difference		332
Per cent increase		41.6

SUMMARY

A stock soil was prepared consisting of five parts of Hagerstown silt loam and one part each of sewage sludge and find sand. The stock soil thus prepared was divided into 10 equal portions of 260 pounds. Nine portions were treated with different amounts of sulfur, and one portion received no sulfur, and all portions were incubated in small field plots for a period of 2 years. At the end of the 2-year period, six of these soils showing the following range in pH—7.4, 7.1, 6.0, 4.5, 3.8 and 3.2 were selected for a study in which soil acidity was the one limiting factor.

The respiratory capacity and organic matter decomposing power of the six soils in relation to acidity were measured in terms of carbon dioxide produced at definite intervals in relation to various organic treatments including cellulose, manure, cotton seed meal, and starch. The influence of the addition of soluble nitrogen dipotassium phosphate, and hydrated lime was also studied. The data include results obtained from both the air-dried soils and those taken later from the small plots and incubated without air drying. The respiration studies were carried out in liter side-neck filter flasks, and the carbon dioxide was measured at 2-day intervals by absorption in a train of soda lime tubes.

The data derived from a study of the soils made acid by the oxidation of applied sulfur, were supplemented with additional studies of limed and unlimed soils which had received similar fertilizer treatment for a period of half a century.

Statistical studies of the method used for the measurement of carbon dioxide showed a probable error of ± 1.95 per cent based on 54 duplicate determinations of the total carbon dioxide produced in 14 days compared to a probable error of ± 5.2 per cent based on 378 duplicate determinations of the carbon dioxide recovered at 2-day intervals. These statistical studies formed a basis for determining the significance of the differences in behavior of the soils of different pH values with respect to the production of carbon dioxide derived from the treated and untreated soils. These studies lead to the following conclusions:

A close correlation was found to exist between the reaction of the six soils and their respiratory capacity and organic matter decomposing power.

The addition of soluble nitrogen to the soils treated with organic materials and to the soil alone caused an increase of carbon dioxide production of all six soils but failed to restore the activity of the acid soils to a degree comparable with that of the soils of pH 7.4 and 7.1.

An application of dipotassium phosphate to the soil + cellulose + nitrogen treatment had little effect either in stimulating carbon dioxide production or in changing the established ratio of the relative cellulose decomposing power of the six soils.

Lime applied to the four acid soils 30 days prior to the respiration studies followed by the cellulose + nitrogen treatment, restored the acid soil to a carbon dioxide production capacity comparable with that of the two alkaline soils.

The process of air drying the six soils greatly stimulated the production of carbon dioxide compared with the fresh screened soil. The relative respiratory capacity and cellulose decomposing power of the two sets of soils, however, were quite similar.

The use of corn starch as a source of organic matter gave results contrary to the data obtained with cellulose, manure, and cotton seed meal. It is concluded that cellulose (ground filter paper) is best adapted for such studies.

The respiratory capacity and organic matter decomposing power of the six soils run parallel with the number of soil microörganisms present, in the case both of the air-dried soils and of those incubated without air drying.

Lime stimulated both the production of carbon dioxide of the acid soils and the number of soil microörganisms.

The limed soils of the old fertilizer plots show a cellulose decomposing power 41.6 per cent in excess of that of the unlimed soils.

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THE SETTLING VOLUME OF SOILS

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The soils of the Erosion Experiment Stations present a number of distinct soil types representative of the Great Soil Groups [Marbut's Classification (5)]. The lateritic soils are represented by the Kirvin fine sandy loam and the Nacogdoches fine sandy loam at Tyler, Texas, and the Cecil sandy clay loam at Statesville, N. C.; the prairie soils are represented by the Shelby silt loam at Bethany, Mo., the Marshall silt loam at Clarinda, Iowa, and the Palouse silt loam at Pullman, Wash.; the chernozem group is represented by the Colby silty clay loam at Hays, Kans.; the Houston black clay is a rendzina soil at Temple, Texas. The gray-brown podzolic soils are represented by the Vernon fine sandy loam at Guthrie, Oklahoma, the Knox[2] silt loam at La Crosse, Wisconsin, and the Muskingum silt loam at Zanesville, Ohio. Descriptions and analytical data on the Knox, Nacogdoches, and Muskingum soils have not been published. Rather full data on all the others have been published (7).

In a study of the erosional characteristics of these soils, Middleton (6) measured what he calls the "dispersion ratio," the relation between the amount of material which, under specific conditions, remains suspended in water and the total silt and clay of the soil. In the seven erosion station soils (7) this value varied for the different horizons between the limits of 5.4 and 41.4 per cent.

While these measurements were being made it was observed that when the suspended soils were allowed to stand in the presence of excess water, very different minimum volumes were reached. These volumes obviously represent a soil water equilibrium system at the maximum water content. It seemed of interest to determine this relation as exactly as possible, in view of the fact that it may be related to the erosional behavior of the soils.

The following procedure was adopted. A quantity of air-dry soil equivalent to 50 gm. of oven-dry soil is put into a 250-cc. beaker, and 35–40 cc. of water is added. The soil and water are vigorously stirred and the beaker is placed in a vacuum desiccator and evacuated until the mixture boils vigorously. The mixture is poured into a 100-cc. graduate with the minimum quantity of water

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[2] In a forthcoming technical bulletin on the erosion station soils this soil type is termed "Clinton silt loam" in order to conform to the present usage of the U. S. Department of Agriculture Soil Survey.

required for rinsing the beaker. The resulting volume is usually about 90 cc. The graduate is covered by the palm of one hand and shaken vigorously. It is then set on the table, the inside washed down with a fine water jet, and the volume made up to 100 cc. The suspension is allowed to stand for 24 hours and

TABLE 1

Settling volume of soils from the erosion experiment stations

SAMPLE NO.	SOIL TYPE AND LOCATION	HORIZON	SETTLING VOLUME	COLLOID BY WATER VAPOR ABSORPTION	MOISTURE EQUIVALENT	WATER SATURATION CAPACITY	APPARENT SPECIFIC GRAVITY OF SOIL IN SUSPENSION ON DRY BASIS	SPECIFIC GRAVITY OF SUSPENSION
			cc.	*per cent*	*per cent*	*per cent*		
6678	Kirvin fine sandy loam,	A	41	5.9	7.9	45.0	1.22	1.77
9	Tyler, Tex.	B	67½	56.6	30.5	98.8	0.74	1.47
6718	Vernon fine sandy loam,	A	44	7.4	9.6	50.2	1.14	1.71
20	Guthrie, Okla.	B	54	21.5	17.7	70.8	0.93	1.58
10362	Knox silt loam, La Crosse,	A	53	13.7	23.9	68.0	0.94	1.58
3	Wis.	B	54	20.3	23.5	71.0	0.93	1.58
9475	Nacogodoches fine sandy	A	48	18.6	14.3	59.6	1.04	1.66
6	loam, Tyler, Tex.	B	59	50.5	25.2	83.0	0.85	1.55
6977	Cecil sandy clay loam, States-	A	53	20.0	20.0	68.0	0.94	1.59
8	ville, N. C.	B	58½	45.7	26.6	80.4	0.86	1.54
6797	Shelby silt loam, Bethany,	A	55	23.1	24.5	72.0	0.91	1.56
8	Mo.	B	67	49.6	34.9	86.8	0.75	1.47
8069	Palouse silt loam, Pullman,	A	56	26.4	25.1	74.6	0.89	1.56
70	Wash.	B	61	35.6	27.8	85.4	0.82	1.52
6842	Colby silty clay loam, Hays,	A	59	32.1	27.3	80.0	0.85	1.53
	Kans.	B	60	30.7	25.2	82.6	0.83	1.52
8736	Marshall silt loam, Clarinda,	A	62	33.9	30.1	86.0	0.81	1.50
7	Iowa	B	68	39.4	31.8	98.4	0.74	1.46
6096	Houston black clay, Temple,	A	63	41.1	30.5	88.4	0.79	1.50
7	Tex.	B	62½	40.2	27.6	87.8	0.80	1.50

the soil volume noted. The graduate is again shaken and allowed to stand 24 hours. The process is repeated until a constant volume is reached; this obtains usually after three or four shakings. The volume is noted to the nearest 0.5 cc. Duplicates agree within 1 cc., and the difference is seldom so great. The line between soil suspension and water is very sharp. Occasionally there

is a suspension of colloid of small magnitude in the supernatant liquid, but, when it finally clears, the flocculated material seldom changes the volume by more than 1 cc. On long standing, indeed for several weeks, the volume of the suspension does not change materially. In some instances anaerobic fermentation produces a gas evolution which causes a slight increase in volume. Occasionally, also, a slight decrease occurs. The appearance of the settled soils from the surface horizon of eight of the erosion station soils is shown in plate 1.

The volume of soil water suspension so obtained evidently represents the maximum volume that soil can maintain "permanently" in the presence of water. It has been carefully measured for the A and B horizons of 10 soils from nine erosion stations. The results are given in column 4, table 1.

In table 1 the soils are listed in the order of the colloid content of the surface horizon, and the colloid content for both horizons, as determined by the water

TABLE 2

Erosion ratios of the surface soils of the Erosion Experiment Stations and the apparent specific gravities of the soils in suspension

SOIL TYPE	APPARENT SPECIFIC GRAVITY OF SOIL IN SUSPENSION ON DRY BASIS	EROSION RATIO
Kirvin fine sandy loam	1.22	50.2
Vernon fine sandy loam	1.14	30.3
Nacogdoches fine sandy loam	1.04	21.7
Knox silt loam	0.94	57.4
Cecil sandy clay loam	0.94	22.9
Shelby silt loam	0.91	28.8
Palouse silt loam	0.89	19.4
Colby silty clay loam	0.85	13.0
Marshall silt loam	0.84	14.2
Houston black clay	0.79	8.1

vapor absorption method, is given in column 5. The moisture equivalent is given in column 6. In column 7 is given the "water saturation capacity,"[3] which is the weight of enclosed water in the settling volume of the soil expressed as the percentage of the weight of the dry soil. This is calculated by subtracting the absolute volume of the oven-dry soil (calculated from specific weight data not given in the table) from the settling volume of the soil and dividing this difference, which numerically corresponds to the weight of the water in the suspension, by the weight of the soil. The quotient $\times$ 100 gives the water saturation capacity expressed in percentage. From the data and the specific gravity may also be calculated the apparent specific gravity of the soil as suspended and the specific gravity of the suspension (columns 8 and 9).

[3] Possibly this term is not well chosen because of possible confusion with "maximum water holding capacity," as used by Hilgard, and "saturated" soils, as used in base exchange studies. No better term, however, has occurred to the writers.

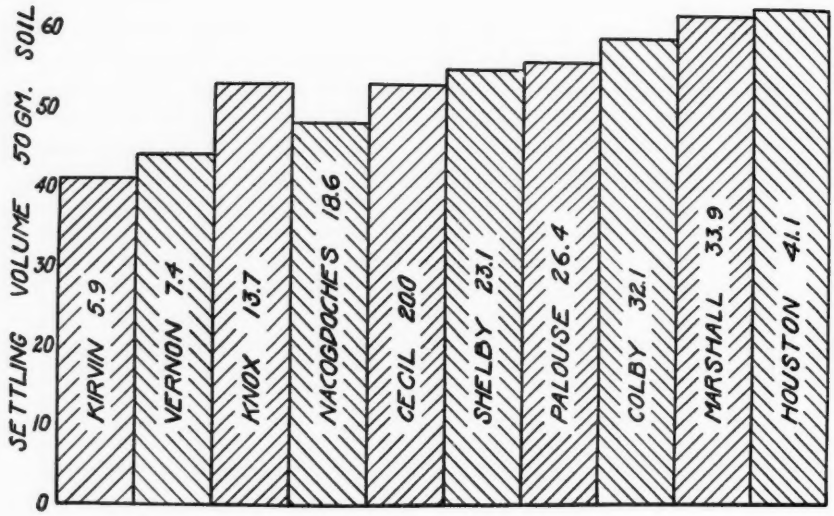

FIG. 1. SETTLING VOLUMES OF A HORIZONS

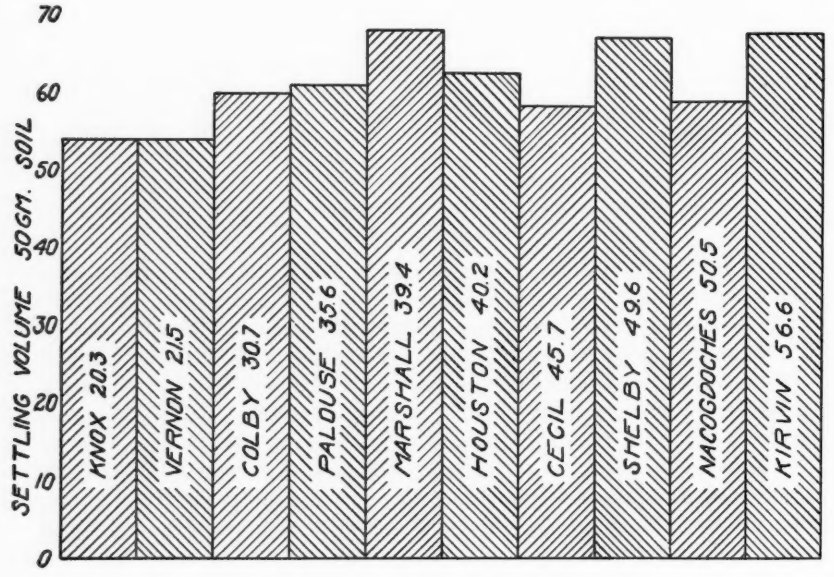

FIG. 2. SETTLING VOLUMES OF B HORIZONS

It might be expected that a certain relation might exist between the erosion ratio (3) and the apparent specific gravity of the soil in suspension; assuming that runoff liquid consists of soil at its water saturation capacity, it would follow that the greater the apparent specific gravity of the soil suspension, the greater the loss of soil per unit of runoff. That there is a qualitative relation may be seen by comparing the erosion ratios of these soils (7) with the quantities given in column 7 as shown in table 2. This relation in itself leaves much to be desired, though in general the high erosion ratios are found for soils with apparent high specific gravity. If we make the same comparison for the B horizon the same trend appears, but with even more erratic variations.

A more satisfactory relation appears when we compare the settling volume (table 1) with the colloid percentage, as is done graphically in figure 1.

TABLE 3

*Mechanical composition and settling volumes of A horizons of the erosion station soils**

SOIL TYPE	MECHANICAL ANALYSIS†			SETTLING VOLUME		DIFFERENCE
	Sand	Silt	Clay	Observed	Calculated	
	per cent	*per cent*	*per cent*	*cc.*	*cc.*	*cc.*
Kirvin fine sandy loam	75.8	15.7	8.6	41	43.8	+2.8
Vernon fine sandy loam	73.3	18.5	8.1	44	44.0	0
Nacogdoches fine sandy loam	69.7	9.8	18.0	48	45.5	−2.5
Cecil sandy clay loam	53.1	20.7	26.2	53	51.4	−1.6
Shelby silt loam	26.0	46.0	27.9	55	55.9	+0.9
Palouse silt loam	6.4	64.0	27.5	56	57.7	+1.7
Colby silty clay loam	18.5	46.5	35.0	59	58.7	−0.3
Marshall silt loam	2.1	59.0	35.3	62	59.4	−2.6
Houston black clay	10.9	26.0	60.4	63	64.4	+1.4

* Knox silt loam had not been received when this portion of the work was completed.

† Determinations by H. W. Lakin and T. M. Shaw.

In this figure the soils are arranged in the order of their colloid content, and the settling volume is charted to scale. With the single exception of the Knox silt loam, the colloid content corresponds qualitatively with the settling volume. This relation is to be expected, since the volume of water absorbed is, as in general moisture relations, greatly affected by colloid content. However, if we make a corresponding chart of the B horizon relations, this harmony of relationship quite disappears (fig. 2). The Shelby soil, with 49.6 per cent colloid, has a slightly smaller settling volume than the Marshall, with 39.4 per cent colloid, whereas the Nacogdoches soil, with essentially equal settling volume with the Cecil and 5 per cent more colloid, has a slightly smaller settling volume than the Colby, with 20 per cent less colloid. Clearly, therefore, the settling volume is not wholly a colloidal effect.

The moisture equivalent is a soil relation which is primarily dependent upon

colloidal content but which, as was shown by Briggs and McLane (3), is partly dependent upon the mechanical components, as expressed by the following equation:

$$0.13\,C + 0.62\,(D + E) = H \pm 3,$$

where C is the silt content and D and E the clay and organic contents, respectively.

In a similar manner the method of least squares applied to the data given in table 3 gives the equation for the surface soils:

$$0.38 \times \text{sand} + 0.53 \times \text{silt} + 0.77 \times \text{clay} = \text{settling volume} \pm 1.29$$

TABLE 4

Mechanical composition and settling volume of B horizons of the erosion station soils

SOIL TYPE	MECHANICAL ANALYSIS*			SETTLING VOLUME		DIFFERENCE
	Sand	Silt	Clay	Observed	Calculated†	
	per cent	*per cent*	*per cent*	*cc.*	*cc.*	*cc.*
Kirvin fine sandy loam	31.1	7.4	61.5	67½	63.0	−4.5
Vernon fine sandy loam	60.3	12.4	27.2	54	50.4	−3.6
Nacogdoches fine sandy loam	45.7	4.9	48.4	59	57.2	−1.8
Cecil sandy clay loam	30.8	12.1	57.1	58½	62.0	+3.5
Shelby silt loam	19.4	27.7	52.9	67	62.8	−4.2
Palouse silt loam	5.9	55.6	37.5	61	60.7	−0.3
Colby silty clay loam	18.8	42.8	38.5	60	59.6	−0.4
Marshall silt loam	1.5	56.5	39.4	69	61.0	−7.0
Houston black clay	9.6	25.1	64.1	62½	66.3	+3.8

* Determinations by H. W. Lakin and T. M. Shaw.

† Calculated by formula for A horizons.

If these quantities are used to calculate the settling volume of the soils the values given in column 6 are obtained and the differences from the values found are given in column 7. This relation is quite satisfactory if taken alone, but becomes much less satisfactory when applied to the corresponding data for the B horizons, as shown in table 4.

If, on the other hand, the distribution is calculated from the data in table 4, the formula becomes.

$$0.45 \times \text{sand} + 0.61\ \text{silt} + 0.72 \times \text{clay} = \text{settling volume} \pm 2.23$$

This result, even for the data in table 4, is not very satisfactory and becomes even less coherent when applied to the surface soils.

It would seem, however, that the soil characteristics which are responsible for the moisture equivalent should be those which produce the settling volume differences. Figure 3 represents an attempt to correlate the moisture equivalent and settling volume relations.

It will be seen that a reasonably close relation obtains for the surface horizons. The relation for the B horizons is less satisfactory. It is clear, then, that other factors than texture enter into the determination of the settling volume, though texture would seem most important.

What part is played by organic matter is difficult to determine, though the soils examined vary widely in organic content. The organic content of the A and B horizons for the 10 soils is given in table 5.

Those soils high in organic matter are usually high in clay content and in colloid content. They are also high in settling volume, but it seems that the effect of organic matter, if any, is masked by the variations in clay or colloid content.

It seems probable that the settling volume should also be influenced by the character as well as by the content of colloid. To determine whether this is the case, the settling volume of the colloids themselves was determined in

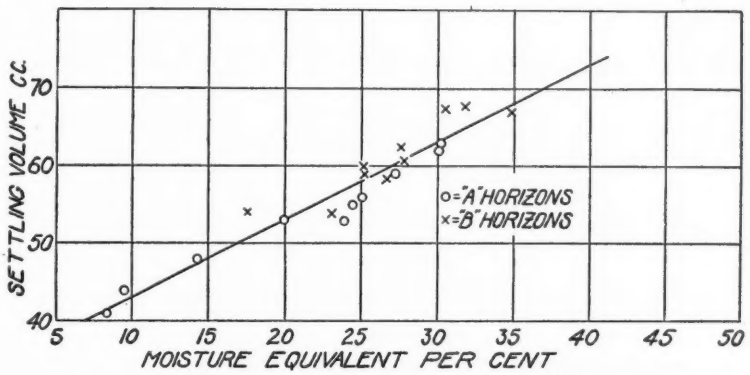

FIG. 3. RELATION OF SETTLING VOLUME TO MOISTURE EQUIVALENT

exactly the same manner as with the soils, except that 10 gm. of colloid were used. The quantity of colloid used is not an important factor, as was shown by using 5, 10, and 25 gm. of the Shelby silt loam colloid with the same volume of water. The settling volumes obtained were 11, 21½, and 53 cc., respectively. It will be seen from these figures that larger quantities of colloid give slightly lower settling volumes per unit weight in this case. Sufficient quantities of colloid were not readily available in the case of the other soil types. The variation, however, is not great, and the comparisons based upon the use of 10 gm. of colloid were considered adequate for the purpose in hand.

The colloids were extracted from the soils, without any dispersing agent, were air dried and rolled to pass a 2-mm. sieve. The determinations were more difficult and less satisfactory than in the case of the soils, since there is a tendency for more of the material to remain in colloidal suspension in all but the carbonate containing colloids. The settling volumes were therefore more

affected by the "volume of floc" as a result of slow flocculation. There was in all cases considerable flocculation. The results obtained are given in table 6.

In this table the colloids are listed in the order of their silica-sesquioxide ratios, which are also given in column 4. In general, it will be observed that the settling volume increases as the silica-sesquioxide ratio becomes greater.

TABLE 5

*Organic content of erosion station soils**

SOIL SERIES	A HORIZON	B HORIZON
	per cent	*per cent*
Shelby	3.23	2.17
Marshall	3.22	2.29
Cecil	3.21	0.45
Houston	2.94	1.88
Colby	2.82	1.11
Palouse	2.18	0.96
Nacogdoches	1.89	1.13
Vernon	1.81	0.62
Knox	1.55	0.59
Kirvin	0.54	0.81

* Determinations by C. S. Slater.

TABLE 6

*Settling volumes of colloids extracted from the A horizons of the erosion station soils**

SOIL FROM WHICH COLLOID WAS EXTRACTED	SETTLING VOLUME	SPECIFIC GRAVITY	SILICA-SESQUIOXIDE RATIO†	WATER SATURATION CAPACITY	APPARENT SPECIFIC GRAVITY OF COLLOID IN SUSPENSION ON DRY BASIS
	cc.			*per cent*	
Nacogdoches fine sandy loam	16	2.92	1.07	126	0.63
Cecil sandy clay loam	19	2.69	1.34	153	0.52
Kirvin fine sandy loam	18½	2.75	2.02	147	0.54
Palouse silt loam	22	2.69	2.48	183	0.45
Shelby silt loam	21½	2.64	2.65	177	0.47
Knox silt loam	22½	2.60	2.69	187	0.44
Marshall silt loam	22	2.62	2.91	182	0.45
Houston black clay	26	2.67	3.26	223	0.38
Colby silty clay loam	24½	2.67	3.45	208	0.41

* Vernon fine sandy loam was omitted because of lack of sufficient sample. Determinations by C. S. Slater.

The relation is not quantitative. The water saturation capacity and the apparent specific gravity, which are quantities derived from the settling volume, follow the same general relation—the one directly and the other inversely.

It is evident that these colloid-water relations are influenced by the compo-

sition of the colloid. That this influence is marked is shown graphically in figure 4.

The three lateritic colloids, the Nacogdoches, Cecil, and Kirvin, have low settling volumes; the prairie colloids group themselves close together; the Knox colloid is from a soil developed in a prairie region, though apparently under forest cover. The two colloids of greatest settling volume both contain calcium carbonate, but also have the highest silica-sesquioxide ratios of the group of soils examined.

That a relation between the composition and the water relationships of soil colloids exists has been pointed out by Anderson and Mattson (2) and the nature of the differences in composition giving rise to these differences in behavior has been discussed by Byers (4). That the relation is not quantitative is to be expected in the light of the data given by Anderson (1) for a series of

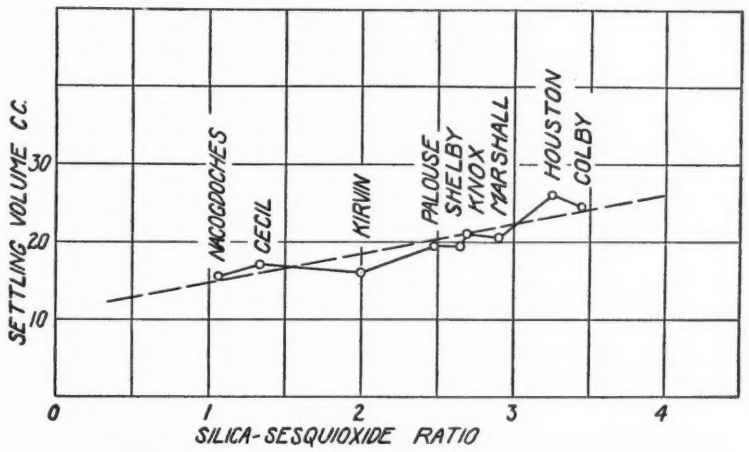

FIG. 4. RELATION OF SETTLING VOLUME OF COLLOIDS TO SILICA-SESQUIOXIDE RATIO

soil colloids ranging in silica-sesquioxide ratios from 0.31 to 3.62. In these colloids marked influence upon the moisture equivalent, swelling, water vapor absorption, and heat of wetting was shown by the bases associated with the colloid.

In the case of the colloids from the erosion experiment stations, the exchangeable bases and the base exchange capacities have not been determined. It is known, however, that these colloids range from the high calcium, high pH, and saturated chernozems to the highly leached lateritic soils. Whether it is possible eventually to trace the extent of the influence of these various factors upon the water relationships of the soils is not yet known.

The investigation of these related properties is, of course, being continued. In the meantime, the relationships shown by the graphs in figure 5 are of considerable interest.

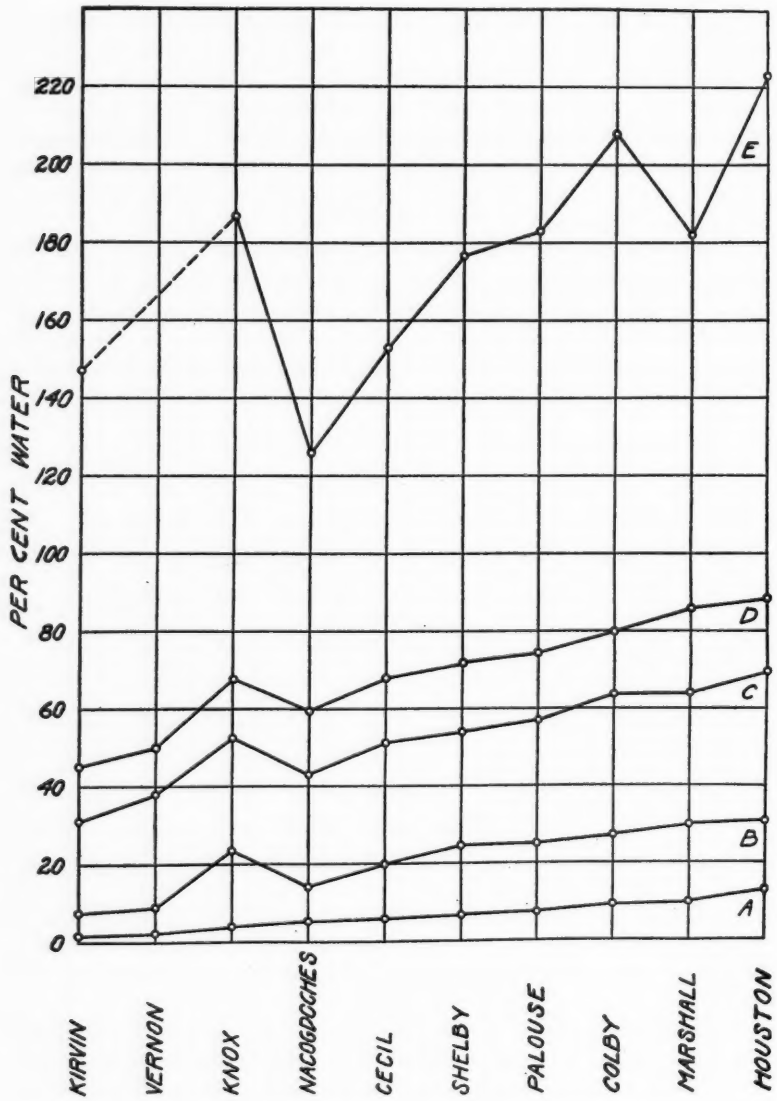

FIG. 5. WATER RELATIONSHIPS OF EROSION STATION SURFACE SOILS

A. Water vapor absorption.
B. Moisture equivalent.
C. Maximum water holding capacity.
D. Water saturation capacity.
E. Water saturation capacity of colloid fraction.

In these graphs the soils are placed, at regular intervals, in the order of their colloid content. The relationship is not quantitative. That the composition of the colloid and the texture of the soil influence all the soil moisture relationships is clear. Perhaps the most interesting thing about the graphs is the abnormal values shown by the Knox silt loam soil with respect to all the properties shown, except the water vapor absorption. That this abnormality is due to the colloid, the water saturation capacity of the colloid clearly shows. Why this colloid, present in relatively small amounts, should be of such marked influence upon the soil behavior is also clearly owing to its silica-sesquioxide ratio, as indicated by the graph shown in figure 4.

We have no clue at present to the inverted relationship of the Colby and Houston colloids and soils. That the soil-water relationship which we have called the "settling volume of soils" is a real and reproducible soil property is made abundantly clear by this figure and the data from which it is developed.

SUMMARY AND CONCLUSIONS

A new soil-water and a new soil colloid-water relation is defined and a method for its determination is described. The relation of this soil property to the colloid, silt, and clay content is discussed, as well as its relation to colloid, composition, organic matter content, and the erosion ratio.

This soil-water relation, the settling volume of soils, is measured for 10 soils of widely different character. The soils are from the Erosion Experiment Stations and their general chemical and physical properties are known.

The term "water saturation capacity" is used to define the percentage water content of the soils at their settling volume, and a comparison is made between this value and the water vapor absorption, moisture equivalent, and total maximum water holding capacity of the soils. It is pointed out that this relation, as far as it is dependent upon colloid composition, is affected not only by the character of the acids and oxides present, and by the organic matter, but also by the kind and quantity of bases present.

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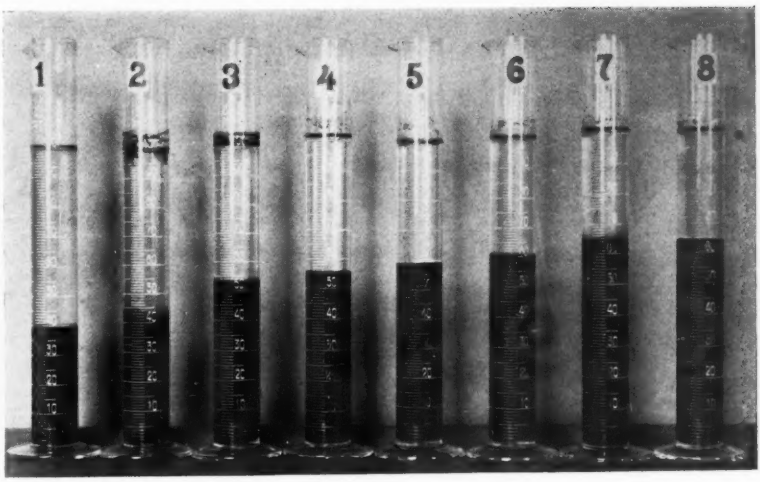
PLATE 1

SETTLING VOLUMES OF A HORIZONS

1. Kirvin fine sandy loam
2. Vernon fine sandy loam
3. Cecil sandy clay loam
4. Shelby silt loam
5. Palouse silt loam
6. Colby silty clay loam
7. Marshall silt loam
8. Houston black clay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AN EXAMINATION OF THE DEGTJAREFF METHOD FOR DETERMINING SOIL ORGANIC MATTER, AND A PROPOSED MODIFICATION OF THE CHROMIC ACID TITRATION METHOD

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Among the many methods of measuring the carbon content of soils two main groups may be recognized: those methods which determine the carbon dioxide produced by oxidation either in the wet or in the dry way, and those which in effect measure the reducing power of the soil by some oxidizing agent. Of the first type of method probably the only one which can be relied upon to give accurate results is the dry combustion method of Liebig or its modification by Dennstedt (3, 4, 5). The various types of wet combustion using chromic acid, though superior in accuracy to most of the methods based on reduction, frequently fail to give the complete oxidation usually claimed for them. The second or indirect type of method is based upon the assumption that carbon is the chief reducing agent present in soils and that any other substance exerting a minor effect will bear a constant proportion to the carbon. Any hydrogen atoms in the organic complex not fully oxidized already are likely to undergo oxidation along with the carbon, whereas nitrogen atoms, in taking up hydrogen to form ammonia, will act in the opposite way, so that one must assume that the proportions of carbon, oxidizable hydrogen, and reducible nitrogen are present in the organic matter of soils in about the same proportions. There is also the possibility of the presence of inorganic substances of an oxidizing or reducing nature, though probably these do not commonly occur.

Since indirect methods rarely give complete oxidation, we must make the further assumption that there is a definite fraction of organic matter common to many different kinds of soil which is readily attacked by oxidizing agents. In support of this there are the results of W. McLean (6), who has shown that 3 per cent hydrogen peroxide removes 85 per cent of the organic matter from a number of soils. Oxidations with sodium hypobromite and with chromic acid behave similarly.

Indirect methods may thus prove useful in the rapid examination of large numbers of soil samples for survey or advisory work when the necessary factor has been established by more exact determinations on typical ones. In the course of a comparative study by one of us on a number of such rapid methods,

[1] The authors wish to express their thanks to Dr. E. M. Crowther for a number of valuable suggestions and for his helpful criticism throughout.

the one proposed by Degtjareff (2) was carefully examined, for we could find no theoretical basis for its action.

In the Degtjareff method 0.15 to 0.2 gm. finely ground soil is treated first with 10 or 15 cc. of 0.3 per cent hydrogen peroxide and then with an equal volume of a solution of 1.6 per cent chromic acid in concentrated sulfuric acid. Considerable heat is evolved. The mixture is shaken for a minute, washed into a beaker, and diluted to about 200 cc. Excess chromic acid is then titrated with ferrous ammonium sulfate in the presence of diphenylamine and from the amount of chromic acid reduced the carbon content of the soil is calculated.

The form of the titration, originally suggested by Schollenberger (8) was subsequently improved by him (9) by the addition of sodium fluoride, which makes the end point much sharper by preventing the buffering action of iron salts. We have used throughout Schollenberger's improved method of titration.

Since chromic acid and hydrogen peroxide react with mutual decomposition it is difficult to see what useful function the peroxide can perform other than that of providing water with which to generate heat when mixed with the strong sulfuric acid solution. It necessarily reduces the strength of the chromic acid, which is in excess, and if any organic matter is oxidized by the hydrogen peroxide or by nascent oxygen from its decomposition, the net result must be to reduce the apparent carbon content, since less chromic acid will then be used up.

With the short interval of contact between soil and the oxidizing agent it seemed most unlikely that oxidation of soil carbon could be complete. It thus appeared probable that some concealed error happened to cancel out the incompleteness of oxidation under the conditions used by Degtjareff. Preliminary trials soon showed that the apparent carbon content fell off rapidly when increasing amounts of soil were used in the determination. Since the work here reported was completed we have received a paper in which Tiurin (10) condemned the Degtjareff method and suggested that the reaction between hydrogen peroxide and chromic acid was incomplete but proceeded further in the presence than in the absence of soil. He produced, however, no direct evidence that any hydrogen peroxide remained in the presence of excess chromic acid, and it can easily be demonstrated that in such solutions no hydrogen peroxide does in fact remain. Ether extracts a deep blue perchromic acid from chromic acid solutions containing hydrogen peroxide, but fails to do so from the Degtjareff solutions (whether with or without soil).

Degtjareff and Tiurin assume that the reaction between hydrogen peroxide and chromic acid in strong sulfuric acid is

$$2\,CrO_3 + 3\,H_2O_2 + 3\,H_2SO_4 = Cr_2(SO_4)_3 + 6\,H_2O + 6\,O \quad \ldots\ldots\ldots (A)$$

The nature of the corresponding reaction in *dilute* acid solutions was the subject of active investigations and discussions about 30 years ago (1, 7). Equation *A* was generally accepted, but an alternative one

$$2\ CrO_3 + 4\ H_2O_2 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 7\ H_2O + 7\ O \quad \ldots\ldots\ldots\ldots (B)$$

was also proposed. The reactions in dilute solutions are naturally no guide to those in strong sulfuric acid solutions, but the possibility of altering the reaction by slight changes in conditions required examination. Our work indicates that soil acts catalytically and leads to the unusual situation that one reaction proceeds in the presence of soil and the other in the blank. The difference between the two parallel determinations with and without soil therefore fails to measure the carbon content of the soil, and it is an odd chance that the excess aparent carbon given by this change in the nature of the reaction should balance out the incompleteness of the actual attack on soil carbon for the conditions under which Degtjareff appears to have worked.

EXPERIMENTAL

The data quoted in this paper refer to determinations made on a standard series of seven representative British Soils selected by the Soil Analysis Sub-Committee of the Agricultural Education Association for coöperative work. All samples were ground in either a porcelain or an agate mortar to pass a sieve with 100 meshes to the linear inch. (It may be mentioned that in any measurement of soil organic matter by reduction of an oxidizing agent such as chromic acid or sulfuric acid, very serious errors may be introduced, especially in sandy soils, if at any stage in the preparation of the sample an iron or steel mortar and pestle are used. Sufficient metallic iron is introduced into the sample to cause reduction comparable with that of a considerable amount of carbon in soil organic matter.)

The Dennstedt (3, 4, 5) method of combustion was used as the standard method for determining organic carbon. The soil was heated in a stream of oxygen, the products of oxidation passing over a heated sheet of platinum to ensure complete oxidation and then over lead peroxide to remove oxides of nitrogen and of sulfur and halogens. The carbon dioxide produced was determined gravimetrically. Inorganic carbon (as calcium carbonate) was present in only one (Rothamsted) of the seven soils. It was removed before the combustion by evaporating the soil to dryness on a water bath with excess of a solution of sulfurous acid. This removed carbonates and left a certain amount of sulfite which was oxidized to sulfur trioxide and absorbed by the lead peroxide in the Dennstedt combustion tube.

No sulfurous acid treatment was needed for the Dennstedt combustions on the six carbonate-free soils or for any of the experiments with chromic acid, for these all measure the reduction of the chromic acid and not the carbon dioxide produced in the course of the reduction.

The details as to strength and preparation of solutions used in the reduction methods are as described by Degtjareff and are given in the following:

(*a*) Hydrogen peroxide—0.3 per cent.

(*b*) Chromic acid—16 gm. CrO_3 is dissolved in a liter of conc. H_2SO_4 and the mixture heated to 165°C. for half an hour to stabilize it.

(*c*) Diphenylamine—0.5 gm. dissolved in 100 cc. conc. H_2SO_4 and 20 cc. water.
(*d*) Ferrous ammonium sulfate—0.2 *N*.

In each of the determinations by the reduction methods 0.15 gm. of 100-mesh soil was put into a 350–cc. flask into which was then pipetted 10 or 20 cc. of H_2O_2, followed immediately by the same volume of chromic acid solution. The mixture after having been shaken for a minute was cooled and diluted to 150:200 cc. Next, 5 gm. sodium fluoride was added and when dissolved titrated with ferrous ammonium sulfate in the presence of 1 cc. of diphenylamine. Blank experiments were carried out under identical conditions.

Table 1 gives the results of the determinations by the Dennstedt method, by the Degtjareff method using two different amounts of reagents, and also by chromic acid with water instead of hydrogen peroxide.

The results of table 1 are plotted in figure 1. It is clear that the Degtjareff method gives excessively high values for low amounts of carbon and progressively decreasing recoveries with increasing amounts of carbon. The apparent recovery reaches 100 per cent for 0.15 gm. of a soil containing about 4 per cent of carbon when 40 cc. of mixed reagents are used in the determination.

TABLE 1

Carbon determinations by the Dennstedt and Degtjareff methods

SOIL	WOBURN	HARPER ADAMS	ROTH-AMSTED	COCKLE PARK	BANGOR	CRAIB-STONE	INSCH
Per cent carbon by dry (Dennstedt) combustion	0.87	0.91	1.87	1.98	3.06	3.88	4.88
Per cent carbon by reduction method using:							
1. 20 cc. H_2O_2 + 20 cc. CrO_3	1.78	1.73	2.89	2.45	3.32	3.97	4.55
2. 10 cc. H_2O_2 + 10 cc. CrO_3	1.06	1.17	1.96	1.74	2.58	2.95	3.28
3. 20 cc. water + 20 cc. CrO_3	0.60	0.73	1.47	1.41	2.24	2.62	3.50

If x represents the percentage of carbon found by combustion and a the apparent percentage of carbon by the Degtjareff method using 0.15 gm. of soil with 20 cc. of hydrogen peroxide and 20 cc. of chromic acid solution, then the regression of a on x is found to be

$$a = 0.70\,x + 1.22$$

Similarly if b is the apparent carbon content when 0.15 gm. of soil is used with 20 cc. of water and 20 cc. of chromic acid solution then

$$b = 0.69\,x + 0.07$$

These two lines are plotted in figure 1. They show that the reduction of chromic acid corresponds to approximately 70 per cent of the carbon present in the soil together with a very large constant for the determinations with

hydrogen peroxide and with a trivial one for those with water instead of hydrogen peroxide. With 40 cc. of mixed reagents for 0.15 gm. of soil, *the Degtjareff method would give an apparent carbon content of 1.2 per cent even if the soil were completely devoid of carbon.*

The determinations with smaller amounts of hydrogen peroxide and chromic acid give results about midway between those just considered, when the soils have little carbon. For the soils rich in carbon the recovery falls off rapidly, since only very small amounts of chromic acid remained available for oxidation

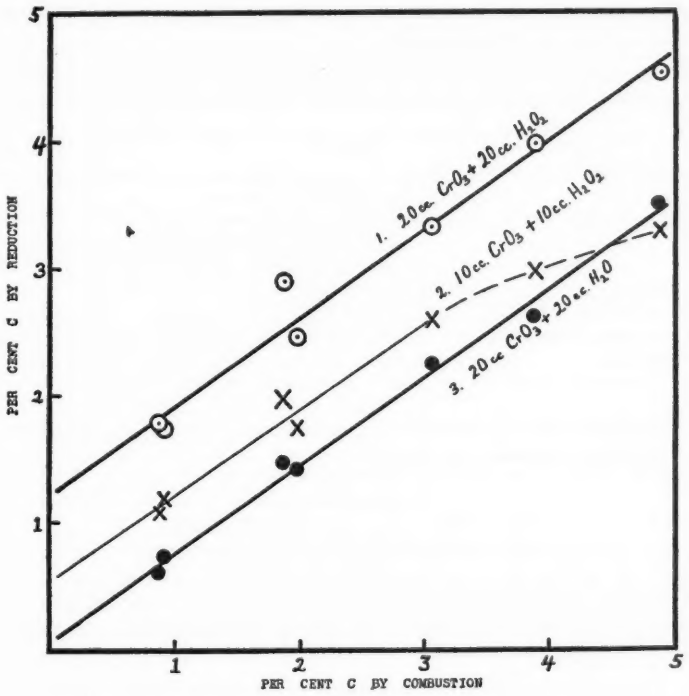

FIG. 1

after the joint reducing actions of the hydrogen peroxide and the large amount of carbon. With these smaller amounts of reagents a soil devoid of carbon would have an apparent carbon content of about 0.6 per cent.

It is clear from these results that the method as recommended by Degtjareff can have no value as an analytical method, and it becomes of interest to examine more closely the cause of its failure.

An attempt was therefore made to determine the quantitative relationships existing in the interaction of H_2O_2 and CrO_3 at the concentrations recommended by Degtjareff both in the presence and absence of soil.

This was done in the following manner:

(*a*) 10 cc. of chromic acid solution was titrated with ferrous ammonium sulfate.
(*b*) 10 cc. of chromic acid was mixed with 10 cc. of hydrogen peroxide and the excess chromic acid titrated as in (*a*).
(*c*) The strength of the hydrogen peroxide was determined by adding to 10 cc. an excess of acidified ferrous ammonium sulfate and titrating back with potassium dichromate.

Table 2 gives the ferrous iron equivalents of the chromic acid (*a*), the hydrogen peroxide (*c*), and the excess chromic acid (*b*) in the mixture of chromic acid and hydrogen peroxide.

To obtain the molecular proportions reacting, these equivalents in terms of iron must be divided by 2 for the hydrogen peroxide, and by 3 for the chromic

TABLE 2

Ferrous iron equivalents of chromic acid, hydrogen peroxide, and excess chromic acid in chromic acid and hydrogen peroxide mixture

	TITRATION VALUE IN CC. 0.2*N* FERROUS AMMONIUM SULFATE	TITRATION VALUE EXPRESSED AS MILLIMOLS FeO	EQUIVALENT IN MILLIMOLS
(*a*) 10 cc. CrO_3	18.25	3.65	1.22 CrO_3
(*b*) 10 cc. H_2O_2 + 10 cc. CrO_3	11.80	2.36	0.79 CrO_3
(*c*) 10 cc. H_2O_2	8.65	1.73	0.86 H_2O_2

acid, as can be seen by considering the following equations, which represent the fundamental reactions occurring:

$$2\,FeO + O \rightarrow Fe_2O_3$$
$$H_2O_2 \rightarrow H_2O + O \therefore 1\ mol\ FeO \equiv \tfrac{1}{2}\ mol\ H_2O_2$$
$$2\,CrO_3 \rightarrow Cr_2O_3 + 3\,O \therefore 1\ mol\ FeO \equiv \tfrac{1}{3}\ mol\ CrO_3$$

Then 0.86 mols H_2O_2 reacted with $1.22 - 0.79 = 0.43$ mols CrO_3, i.e. 2 mols CrO_3 reacted with 4.0 mols H_2O_2. A subsequent independent determination gave the ratio as 2:3.8.

In these cases the peroxide was added to the chromic acid (which was in excess). When the reagents were mixed in the reverse order (as in the Degtjareff method) there was a temporary excess of peroxide in the early part of the reaction, which might possibly be expected to result in a ratio considerably less than 2 CrO_3:4H_2O_2. The ratio found, however, was 2:4.2.

In the absence of soil therefore the reaction appears to be substantially that represented by the equation

$$2\,CrO_3 + 4\,H_2O_2 + 3\,H_2SO_4 = Cr_2(SO_4)_3 + 7\,H_2O + 7\,O \ldots\ldots\ldots (B)$$

When the hydrogen peroxide and the chromic acid were mixed in the presence of ignited soil it was found that the same amount of peroxide reduced more

chromic acid, as shown in table 3. Here 0.84 mols H_2O_2 reacted with 1.10 − 0.55 = 0.55 mols CrO_3, i.e. 2 mols CrO_3 reacted with 3.1 mols of H_2O_2 in the presence of ignited soil as contrasted with 4.0 mols of H_2O_2 in the absence of soil.

With ignited soil, then, the reaction may be represented by the equation

$$2\ CrO_3 + 3\ H_2O_2 + 3\ H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6\ H_2O + 6\ O \quad \ldots\ldots\ldots (A)$$

which was assumed by Degtjareff and Tiurin to hold both for the blank and for the actual determination on soil.

In a blank determination similar to that in table 2 and following equation *A*, the aforementioned amounts of reagents would react so that 1.10 millimols of CrO_3 + 0.84 millimols of H_2O_2 leave $1.10 - \frac{1}{2}(0.84) = 0.68$ millimols of CrO_3 instead of 0.55 millimols of CrO_3. This difference, 0.13 millimols CrO_3 corresponds to an apparent carbon content of the ignited soil of 0.8 per cent and is

TABLE 3

*Ferrous iron equivalents of chromic acid, hydrogen peroxide, and chromic acid, hydrogen peroxide, and ignited soil mixtures**

	TITRATION VALUE IN CC. 0.2*N* FERROUS AMMONIUM SULFATE	TITRATION VALUES EXPRESSED AS MILLIMOLS FeO	EQUIVALENT IN MILLIMOLS
(*a*) 10 cc. CrO_3	16.50	3.30	1.10 CrO_3
(*b*) 0.15 gm. ignited soil + 10 cc. H_2O_2 + 10 cc. CrO_3	8.25	1.65	0.55 CrO_3
(*c*) 10 cc. H_2O_2	8.45	1.69	0.84 H_2O_2

* The hydrogen peroxide and the chromic acid solutions used here were not those mentioned in table 2, but differed only slightly in concentration.

thus of the same order as the figure 0.6 per cent for the apparent carbon content of a soil devoid of carbon as obtained by extrapolation from the middle curve in figure 1.

The error caused by ignited soils appeared to be almost independent of the amount of soil taken.

Thus, a series with 0.07, 0.15, and 0.30 gm. of ignited soil with 20 cc. of mixed reagents gave excess chromic acid equal to 2.0, 2.1, and 2.2 cc. respectively of 0.2 *N* ferrous ammonium sulfate solution over and above the true blank. A little ferric oxide gave excess chromic acid equal to 1.7 cc.

The agreement between the values calculated from soils and those found directly for ignited soils is close enough to establish the disturbance of the reaction by soil, whereas the fluctuations in the actual value of the excess are sufficiently great to invalidate the Degtjareff method even if an attempt were made to improve it by allowing, first, for the essential difference between the reactions in the presence and the absence of soil, and second, for the incompleteness of the actual oxidation.

A PROPOSED MODIFICATION OF THE CHROMIC ACID TITRATION METHOD

From the parallelism of the lines for carbon recoveries in figure 1 it is clear that the oxidation of soil carbon proceeds just as far with chromic acid and water as with chromic acid and hydrogen peroxide and in addition that the line for the recovery with chromic acid and water passes so close to the origin that the apparent carbon contents are proportional to the true carbon contents. Although it is clearly impossible to base a rapid method on the use of chromic acid plus hydrogen peroxide, it should be possible to do so by the chromic acid plus water method provided it can be shown that the fraction of the total carbon recovered is reasonably constant for the groups of soil tested. Evidence for this possibility is afforded by Schollenberger's original proposal to determine carbon by treating a small amount of soil with 2 per cent potassium dichromate in strong sulfuric acid and heating to 175°C. in 90 seconds; by the work of Vassiliev (11), who used a slight modification of Schollenberger's method; and by Tiurin's method of treating the soil for 5 minutes with a boiling solution of chromic acid in 1:1 sulfuric acid and water. A considerable simplification in such methods may be effected by using the heat of reaction between sulfuric acid and water to avoid the necessity of external heating. This was the essential feature of Degtjareff's proposal though the principle was obscured and the method invalidated by using dilute hydrogen peroxide instead of water. There is a considerable advantage, however, in replacing the chromic acid-sulfuric acid solution, which is somewhat unstable, troublesome to make up, and difficult to measure out accurately, by aqueous potassium dichromate, which is free from these disadvantages. The necessary heating and acidity are obtained by adding sulfuric acid. Further work on the details of the method and on the significance of the readily oxidized fraction is in progress. In its present form the method is as follows. Finely divided soil, passing a 100-mesh sieve, is taken in amounts containing between 10 and 25 mgm. of carbon and placed in a 350-cc. conical flask. About 10 cc. of *N* potassium dichromate is then added from a burette, followed by 20 cc. of strong sulfuric acid, which is run in from an automatic pipette. The mixture is shaken for about 1 minute. After it has been cooled and diluted to about 150 cc., 5 gm. of sodium fluoride is added and the chromic acid remaining is titrated with 0.4 *N* ferrous ammonium sulfate, 1 cc. of $\frac{1}{2}$ per cent diphenylamine being used as indicator. Should the end-point be overshot, the mixture can be back-titrated with the potassium dichromate solution used as oxidant.

For a series of 20 British and foreign soils examined by this procedure about 76 per cent of the carbon was accounted for by the reduction of chromic acid. The actual recoveries ranged from 60 to 86 per cent, the standard error being ± 5.6 per cent. A correction factor of $100/76 = 1.32$ must thus be used (1 cc. *N* potassium dichromate equals $1.32 \times 3.0 = 4.0$ mgm. carbon).

Apart from the possible practical value of such an extremely rapid and simple titration method for approximate determinations of soil carbon, it is of

interest to have additional evidence that in soils of similar types the readily oxidizable organic matter forms an approximately constant fraction of the total organic carbon. In addition, the course of the oxidation of organic matter seems to be substantially the same for all of the British soils already discussed, since direct determinations of the products of oxidation showed that about 60 per cent of the total carbon went to carbon dioxide and about 3 per cent to carbon monoxide. This would suggest the almost complete oxidation of a group of compounds common to all of these soils.

SUMMARY

The chromic acid-hydrogen peroxide method of Degtjareff for the rapid determination of soil carbon is shown to give entirely fictitious results.

The hydrogen peroxide not only serves no useful purpose but introduces a fundamental error, since its reaction with chromic acid follows a different course in the determination with soil from that in the corresponding blank.

Two molecules of CrO_3 react with four molecules of H_2O_2 in the absence of soil but with three in the presence of soil or ignited soil. The gain in apparent carbon through this error approximately balances the incompleteness of oxidation for the conditions under which Degtjareff appears to have worked.

A new approximate method giving about 76 per cent recovery of carbon is proposed. Finely divided soil is treated with standard potassium dichromate and twice the volume of sulfuric acid added to raise the temperature; after being stirred for a minute the mixture is diluted and the excess dichromate titrated.

This procedure is more rapid than others so far proposed and it is believed that it may prove useful for comparative purposes where no very exact determination is required.

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A CRITICAL EXAMINATION OF ANALYTICAL METHODS USED IN THE DETERMINATION OF EXCHANGEABLE POTASSIUM AND SODIUM OF SOILS

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Exchangeable potassium and sodium of soils form as a rule not even 10 per cent of the total exchangeable bases, which is an extremely minute quantity, the determination of which is correspondingly difficult. As such, the methods used should be free from errors which have a cumulative effect. The "Proposed Methods" of the Second Commission of the International Society of Soil Science (24), as also those of Kelly and Brown (14) and of Hissink (11), give no details whatever of the determination of the exchangeable alkalies beyond a cursory reference to "usual methods." Russell (18), Schollenberger and Driebelbis (21), Smith (22), and Gedroiz (8, 9) have adopted methods which differ in all details and none of which can claim to be beyond criticism.

Until the Barber and Kolthoff (1) direct method of determining sodium appeared in 1928, and was later extensively tested by Bray (3) and subsequently by Rice Williams (27) with special reference to the determination of exchangeable sodium, the exchangeable alkalies used to be separated and weighed as mixed chlorides or sulfates, in which the potassium was subsequently determined and sodium calculated by difference. The methods of separation were extremely cumbersome and time-consuming, and in the preliminary stages of certain base exchange studies on soils of eastern England (19) involving considerable analytical determinations of the exchangeable alkalies, all the available methods discussed in the following were examined and found to be unsatisfactory, especially for routine work. Of these, Gooch and Eddy's method (10a) of separation, so far not employed in the determination of the exchangeable alkalies, seemed to be the best then available, and was used for certain soils derived from Jurassic and Cretaceous sediments (19). Finally by using ammonium acetate as the replacing agent instead of ammonium chloride, an extremely simple technique adapted for routine determinations was developed for the direct determination of exchangeable sodium by the

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Barber and Kolthoff method (1), and of potassium by the volumetric-cobaltinitrite method, with an immense saving of time and gain in accuracy.

METHODS USED FOR THE DETERMINATION OF EXCHANGEABLE SODIUM AND POTASSIUM

Russell's method. The method suggested by Russell (18) is most unsatisfactory on both theoretical and practical grounds. After the separation of calcium, sodium is determined by weighing the mixed chlorides or sulfates of magnesium, potassium, and sodium, and subtracting the values found separately for the first two. The sources of error are: (*a*) Magnesium cannot be separated as an anhydrous chloride, as it is well known that on evaporation on the water bath it forms basic magnesium chloride, Mg(OH)Cl, which on heating forms an oxychloride Mg_2OCl_2, decomposing easily into the oxide MgO (14b). Even as sulfate the same difficulties occur; $MgSO_4$ containing seven molecules of water and being a salt dehydrates only at 200°C., beyond which it tends to decompose into the oxide; (*b*) Sodium is here estimated by subtracting the values of two quantities both occurring in minute amounts, errors in the determinations of which will make the result for sodium all the less trustworthy: and sodium is an element which requires the most exact evaluation in view of the rôle it plays in the physical and chemical properties of soils.

Schollenberger and Driebelbis (20) adopt quite a different and tedious procedure. After the separation of calcium by oxalate and the magnesium by ammonium arsenate, the alkalies are determined by evaporating the residue to dryness and converting to sulfates, and expelling the ammonium salts and arsenic. The residual sulfates of the alkalies are filtered off from any insoluble matter (mainly silica) into a 100-cc. Pyrex beaker, evaporated, ignited, and weighed. The potassium is precipitated as K_2PtCl_6, excess plantinic chloride is dissolved in 80 per cent alcohol in a Gooch crucible, the sulfates are removed with half-saturated ammonium chloride, and the latter is removed by final washing with alcohol. From the amount of potassium the sodium is calculated by difference.

This method, with further details and numerous corrections omitted in the foregoing description, is too cumbersome and is even more time-consuming than the method of Gedroiz which is described later. Needless to say, the sodium determination is loaded with all the errors of the analysis, and its accuracy is dependent upon the most thorough separations, and more than all upon the use of extremely pure reagents used only in minimum amounts. The filtrate is bound to be contaminated with sodium salts all through the different stages, in amounts that may have a cumulative effect that will seriously affect the results. It is difficult to conceive how a blank could be carried out under identical conditions, using all the reagents in corresponding amounts.

Gedroiz's method (8, 9), followed by A. M. Smith (22) in his study of the

exchangeable bases of Scottish soils, and presumably by most workers, has much to be said in its favor, except that it is too long and that for the separation of all metals except the alkalies milk of lime is used, a reagent which one may doubt could be obtained in an extremely pure form totally free from traces of alkalies compared to ammonium carbonate used in Gooch and Eddy's method (see the following section).

Gedroiz removes the excess of ammonium chloride used for leaching by treatment with concentrated nitric acid on the water bath and the nitrates are then converted to chloride by repeated evaporation with concentrated hydrochloric acid. The alkali chlorides are separated by precipitation of magnesium, iron, aluminum, and manganese with milk of lime (note that the latter three bases always occur in extracts from acid soils); then the calcium is precipitated in the filtrate by repeated treatment with ammonium carbonate and ammonia, warmed on the water bath, followed by filtration. The last process has to be repeated several times and the final traces of calcium must be removed with boiling ammonium oxalate. The separation is obviously tedious and hardly adapted for routine work. Smith (22), who uses the perchlorate method for estimating potassium, removed sulfate with baryta at first, and then separated the rest by repeated precipitation with ammonium carbonate. He did not use milk of lime as Gedroiz does. As discussed in the following, it is questionable whether complete precipitation can be brought about by ammonium carbonate in *aqueous* solution. After the separation of the alkalies, the carbonates are converted to chlorides by repeated evaporations with hydrochloric acid, dried at 100°C., and the last traces of ammonium chloride expelled by ignition, the residue is dissolved in water, filtered from any separated silica, and the mixed chlorides are evaporated, dried gently, ignited, and weighed as KCl + NaCl.

Gooch and Eddy's method for separation of the alkalies. This method, though unique in contrast to the laborious methods described and the extremely unreliable method suggested by Russell (18), has not been adopted in the determination of the exchangeable alkalies as shown by the literature. The separation is claimed to be complete and can be carried out in one operation. It was adopted in the earlier stages of the base exchange studies previously mentioned after the details suggested by Husband and Godden (13), and was found by them to be accurate for the determination of the sodium and potassium in feeding stuffs. The method is that of Kramer (14a) for the determination of sodium and potassium in blood after the method worked out by Gooch and Eddy (10a). The modified method suggested by Husband and Godden is meant to avoid errors arising from the incomplete removal of magnesium. This is overcome by evaporating the solution to dryness before precipitation with *alcoholic* ammonium carbonate (Gooch and Eddy's solution). The method depends on the fact that *alcoholic* ammonium carbonate as recommended by Gooch and Eddy brings about complete precipitation in one operation of all the metals except the alkalies.

In applying the method to the separation of the exchangeable alkalies, the ammonium chloride used for leaching was removed by means of concentrated nitric acid and then evaporated with concentrated hydrochloric acid to dehydrate silica and convert nitrates to chlorides. The residue was taken up in water, neutralized with a few drops of strong ammonia, filtered, and evaporated nearly to dryness to form a thick paste. To this when cold 30 to 35 cc. of Gooch and Eddy's solution was added and well stirred with a glass rod. (Gooch and Eddy's solution is prepared by diluting 180 cc. of strong ammonia —SG.88—to 1 liter with water and mixing it with 1 liter of 90 per cent alcohol. In this mixture 250 gm. of pure ammonium carbonate is dissolved by warming. When cold the solution is filtered and is ready for use. It is desirable to store the solution in Pyrex glass bottles, as ammoniacal solutions dissolve appreciable quantities of sodium from the glass.) The dish is covered with a watch glass, allowed to stand 2 hours, preferably overnight, and then filtered through a Whatman No. 42 filter paper into a small beaker. The precipitate is washed

TABLE 1

Exchangeable sodium determined by (a) Gooch and Eddy's modified method and (b) the direct method of Barber and Kolthoff

Soil 22: Ampthill Clay

HORIZON	MILLIGRAMS EQUIVALENTS PER 100 GM. SOIL	
	(a)	(b)
Top soil	0.58	0.063
Subsoil	1.64	0.044
1′ 6″ to 2′ 6″	2.42	0.323
2′ 6″ to 3′ 6″	2.74	0.396

with Gooch and Eddy's solution, redissolved in a few drops of concentrated hydrochloric acid, neutralized with ammonia, and reprecipitated and washed again. The combined filtrates are evaporated to dryness in a weighed vitreosil dish. The residue is dried and the mixed chlorides are converted to sulfates by heating twice with a few cubic centimeters of pure concentrated sulfuric acid, and the excess of acid is removed by gentle ignition on the sand bath. The dry residue is finally heated in the naked flame, and then in the muffle furnace for 10 minutes, and weighed as the mixed sulfates ($K_2SO_4 + Na_2SO_4$). It is preferable to weigh as sulfates, as these are practically non-volatile compared to the chlorides of the alkalies. Further, as the potassium is determined by the volumetric cobaltinitrite permanganate method, sulfates do not interfere. Blank determinations were carried out with the reagents, "B. D. H"-A. R. reagents being used throughout.

Though the foregoing method is the best of the separation methods available, it was infrequently noted that the residue was stained with iron, an observation confirmed by Blenkinsop (2). The doubt as to the absolute efficiency of the

procedure is always present, and the gravimetric data finally obtained for sodium, especially when these are in the order of a few milligrams, are none too convincing. This is illustrated by the results of table 1 for exchangeable sodium determined by this method and the direct uranyl-zinc-acetate method of Barber and Kolthoff (1), using a technique described later.

METHODS PROPOSED

Finally the methods described in the following were adopted with an immense economy of time and a distinct gain in accuracy and are recommended as being quite reliable.

Ammonium acetate was used as the replacing agent instead of ammonium chloride. This reagent introduced by Schollenberger (20) into base-exchange work has immense practical and theoretical advantages detailed by him (20, 21). Its unique practical advantages with special reference to the determination of exchangeable alkalies are: (*a*) the ease with which it can be removed on the water bath, in contrast to the very unpleasant procedure of removal of excess ammonium chloride by ignition or by treatment with concentrated nitric acid; (*b*) it does not tend to creep over the edges of the evaporating dishes as does ammonium chloride; (*c*) the high degree of purity and the ease with which it can be prepared, and in particular the freedom from even traces of sodium salts, whereas on the other hand even the best grade ammonium chloride used ("B. D. H"-A. R.) was found to be contaminated with considerable amounts of sodium salts, a fact confirmed by Piper (17); (*d*) the ease with which an aqueous extract of the alkali carbonates can be prepared from the replaced acetates of the bases, as detailed later.

"B. D. H"-A. R. ammonium acetate was used when it was freshly prepared. Blank determinations did not show the slightest traces of sodium, but after it had been kept a while it was noticed that amounts of sodium, appreciable compared to the exchangeable sodium, were dissolved from the glass. Consequently required amounts of fresh solutions were always prepared and a series of determinations quickly carried out.

The blank for potassium was always significant, and in all samples examined the blank had to be taken into consideration.

In the aqueous extracts prepared as detailed in the following, potassium was separately determined in duplicate by the volumetric-cobaltinitrite-permanganate method, and the sodium determined directly in two other duplicates by the uranyl-zinc-acetate method.

PREPARATION OF EXTRACT

The solutions for the two separate determinations were prepared by the following simple technique:

The whole of the 500 cc. of ammonium acetate from 25 gm. of soil (these amounts were found by preliminary trials to be sufficient for complete removal of exchangeable potassium) was evaporated on the water bath, when the ammonium acetate was removed by volatiliza-

tion. When the evaporation was complete the residue was transferred into a small porcelain dish, re-evaporated to dryness, the dish dried at 110°C. and then over a Rose burner, and when finally dry gently ignited over a small naked flame, at as low a temperature as possible. Because of the minute amounts of potassium and sodium to be determined the final ignition was not carried out in the muffle furnace as was done by Bray and Willhite (4) and Rice Williams (27) in the application of a similar procedure for the determination of the total exchangeable bases of soils. The organic matter very easily burned off, and the acetates were converted to carbonates. When the residue was cool the potassium and sodium were extracted with hot water: the procedure adopted was to moisten the dry residue with water to form a paste, which was finely triturated with a small pestle, and finally extracted with boiling water. In this process the sodium and potassium carbonates are separated from the insoluble residues of calcium and magnesium carbonates. The residue on the filter paper is well washed and the aqueous filtrates are collected in small beakers, ready for the determination of the potassium and sodium.

This extremely simple technique of preparing the solution, associated with the use of ammonium acetate, ensures an immense saving of time, as the processes of ignition and extraction never took more than 1 hour, during which time a whole series of determination can be carried out. The low temperature of ignition and the ease of volatilization of ammonium acetate prevent the serious errors in exchangeable potassium determinations discussed in the following; the potassium is also in the form of the stable carbonate compared to the easily volatile chloride.

For the sodium determination an aqueous solution containing no more than traces of alkaline earths is obtained, in contrast to the technique of Bray (3) and of Rice Williams (27), who take up the ignited residue in hydrochloric acid, neutralize it with ammonia, and thus obtain a solution containing minute amounts of sodium in the presence of "large excess of calcium and magnesium in the form of chlorides." Though the Barber and Kolthoff method for the determination of sodium works in the presence of calcium and magnesium, it would no doubt be an advantage to have a solution containing as small an amount as possible of these salts in the presence of sodium. Besides there is the certain possibility that traces of sodium are not introduced from the hydrochloric acid and ammonia used in the preparation of the extract by the aforementioned authors.

RELIABILITY OF EXCHANGEABLE POTASSIUM FIGURES

The question of the estimation of potassium in soils (and it applies with equal emphasis to exchangeable potassium in soils) has received a good deal of attention during recent years. The most popular methods a few years ago were the perchlorate and the platinic chloride methods, though both these are susceptible to a complexity of errors unlike the cobaltinitrite method when applied to soil extracts. Dodd (6) drew attention to the several sources of error in both the former methods, and strongly urged the adoption of the volumetric-cobaltinitrite method as the official method. When applied to small quantity work, such as the determination of 5 to 10 mgm. of exchangeable potassium,

in the presence of small quantities of calcium sulfate, which invariably occur in minute but appreciable amounts in the soil extract, a gravimetric method is beset with many difficulties compared to a volumetric method.

In the earlier stages of the work on base exchange studies previously mentioned, the details followed in applying the volumetric-cobaltinitrite permanganate method to the determination of exchangeable potassium were those modified by Morris (16) after the original method of Adie and Wood (a1). The exchangeable potassium was determined in the mixed sulfates separated by Gooch and Eddy's method previously described. Later when Milne (15) published his modification of the method as applied to soil extracts, his technique was adopted.

Milne (15), in applying the method to the determination of exchangeable potassium using ammonium chloride, called attention to the possibility of serious error in the values obtained. Adding known amounts of potassium in the form of potassium chloride to the ammonium chloride extracts of two soils, he was able to recover only 60 to 80 per cent of the added amounts, as shown in table 2, after the excess of ammonium salts had been removed, though with

TABLE 2

Recovery of potassium from ammonium chloride extracts

	DIFFERENT ESTIMATE ON SIMILAR ALIQUOTS OF AN NH_4Cl EXTRACT	PER CENT RECOVERY OF ADDED AMOUNTS
Soil C (sandy loam)	6.13, 5.56, 5.95 mgm. K_2O	77, 88, 85
Soil D (chalk soil)	9.89, 9.17, 9.26, 8.12, mgm. K_2O	61, 77

citric acid extracts no evidence of serious inaccuracies were observed, 96 to 97 per cent of the added potassium being recovered. Though he does not state the method used for removing the excess of ammonium chloride, Milne suggested that it may be associated with the method of destroying a large quantity of ammonium salts, when an appreciably volatile constituent, such as potassium chloride, is to be estimated in the residue. Presumably he had adopted the method of ignition, and losses of potash are bound to occur where potash exists in the form of chlorides subjected to prolonged ignition or even where the ammonium chloride is removed with concentrated nitric acid followed by subsequent ignition. Rice Williams (26), too, subjects the residues to a prolonged ignition of several hours, after preliminary removal of acetic acid used as the replacing agent by evaporation with hydrochloric acid, or ammonium chloride with concentrated nitric acid and subsequent ignition, before obtaining the aqueous extract for the potassium estimation by Milne's method.

As this was an extremely important point to be critically tested, it was decided to investigate whether such losses occur when ammonium acetate is used as the replacing agent, in view of the theories as to the important rôle of ex-

changeable potassium in plant nutrition held by several workers within recent years, such as Hoagland and Martin (12), Fraps (7), Gedroiz (10), Burd (5), Stewart (23), and Wheeting (25), to mention only a few, which necessitate the accurate estimation of exchangeable potassium.

Nine 25-gm. lots of a heavy Oxford clay subsoil (pH 6.7) were extracted with normal ammonium acetate to 500 cc. each. In three the exchangeable potassium was determined in the aqueous extract prepared as previously described. To three of the remaining ammonium acetate extracts before evaporation and ignition, 25 cc. of a solution of potassium chloride containing 5.069 gm. K_2O was added and to the remaining three, 50 cc. of the same solution containing double the amount of potassium. After evaporation and ignition as previously described, the potassium in the aqueous extracts was determined by the volumetric-cobaltinitrite-permanganate method using Milne's technique. Table 3, which is self-explanatory, shows that *there is practically*

TABLE 3

Exchangeable potassium and the recovery of added potassium from ammonium acetate extracts of an Oxford clay soil

	K_2O FOUND	MEAN OF 3 TRIALS	ADDED K_2O RECOVERED	
	mgm.	*mgm.* K_2O	*mgm.*	*per cent*
1. Exchangeable potassium	5.16 5.18 5.17	5.17	....	....
2. Exchangeable potassium with added KCl = 5.069 mgm. K_2O	9.95 10.17 10.23	10.12	4.95	97.6
3. Exchangeable potassium with added KCl = 10.14 mgm. K_2O	14.97 15.22 15.16	15.12	9.95	98.1

complete recovery of added potassium and that the method is extremely trustworthy. As previously suggested this may be also due to the fact that potassium is converted from the acetate to the stable non-volatile carbonate—an observation supported by the fact that Milne obtained 96 to 97 per cent recovery in the case of added potassium determined in citric acid extracts of soils, where the potassium citrate is finally converted to carbonate during ignition.

In using Milne's technique it was found extremely convenient and rapid to filter and wash the precipitate in Jena glass filters (grade of porosity 4, capacity 30 cc.), which are undoubtedly preferable to the Gooch crucible with a disc of filter paper pressed well down at the edges and covered with glass dust as recommended by Milne. A distinct advantage was the fact that these could be repeatedly used with equal efficiency and are easy to clean. The permanganate oxidation was done in 800-cc. Pyrex glass beakers. Excellent duplicates were always obtained, as shown in table 3.

THE DETERMINATION OF EXCHANGEABLE SODIUM

When the mixed alkali sulfates were separated by Gooch and Eddy's method, as previously described, sodium was found by difference after the estimation of potassium. This was abandoned in the later stages of the work and the sodium was directly determined in the aqueous extract prepared as described before by the direct uranyl zinc acetate gravimetric method of Barber and Kolthoff (1).

As this method has been exhaustively examined by Bray (3) and by Rice Williams (27) as applied to the determination of exchangeable sodium of soils, a further examination was considered unnecessary.

SUMMARY

Analytical methods used in the determinations of exchangeable potassium and sodium of soils are critically reviewed, and the unsatisfactory nature of the methods mentioned in the literature is emphasized. As these bases occur in minute amounts in the absorption complex compared to the alkaline earth bases, accurate and standardized methods are necessary in view of the important rôle exchangeable sodium and potassium play in soils.

It is shown that the ammonium acetate as a replacing salt for the determination of exchangeable potassium gives very reliable results in contrast to the errors associated with the use of ammonium chlorides as observed by Milne. An extremely simple and rapid technique is described.

The determination of exchangeable sodium by the method of Barber and Kolthoff is recommended.

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AN ELECTROMETRIC-TITRATION METHOD OF FINDING THE pH VALUE AND LIME REQUIREMENT OF SOILS

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The use of the antimony electrode for determining soil reaction has been advocated by several workers,[1] though so far it has not found much favor with the majority of soil scientists. The antimony electrode is simple in operation, but its uniform response to changes in reaction throughout the working pH range has not been generally or sufficiently appreciated.

The erratic behavior of the antimony electrode is definitely traceable to a poorly polished surface. *Since the successful working of this electrode depends on a perfectly smooth and polished surface, after every determination it should be polished with fine emery powder on cloth;* or simply with a clean strip of filter paper.

The usual electrometric method of finding pH value of solutions requires a potentiometer and a sensitive galvanometer. A good potentiometer is an expensive piece of apparatus requiring careful handling. In this paper a simpler technique is described which does away with the potentiometer and makes use of the galvanometer only.

The principle of the method is well known and has been used in a modified form, in the case of the hydrogen electrode. It depends upon the fact that two antimony rods in solutions having the same pH value develop the same potential and if connected together through a galvanometer no current will be shown to be passing. Thus if two antimony electrodes are dipped, one in a solution of unknown reaction and the other in a buffer solution the pH value of which could be altered gradually by the addition of acid or alkali, and the two are connected together through a galvanometer, as shown in figure 1, then the pH value of the unknown solution could be determined by adding gradually acid or alkali to the buffer solution and tapping the galvanometer each time till the zero point is reached. The pH value of the unknown solution will then be equal to that of the buffer solution and can be read from the titration curve of the latter.

EXPERIMENTAL

Two points are important for the success of the method outlined in the foregoing, namely, the choice of the buffer solution, the titration curve of which

[1] Puri, A. N. 1932 The use of the antimony electrode for determining soil reaction. *Mem. Punjab Irrigation Res. Inst.* vol. 4 (4).

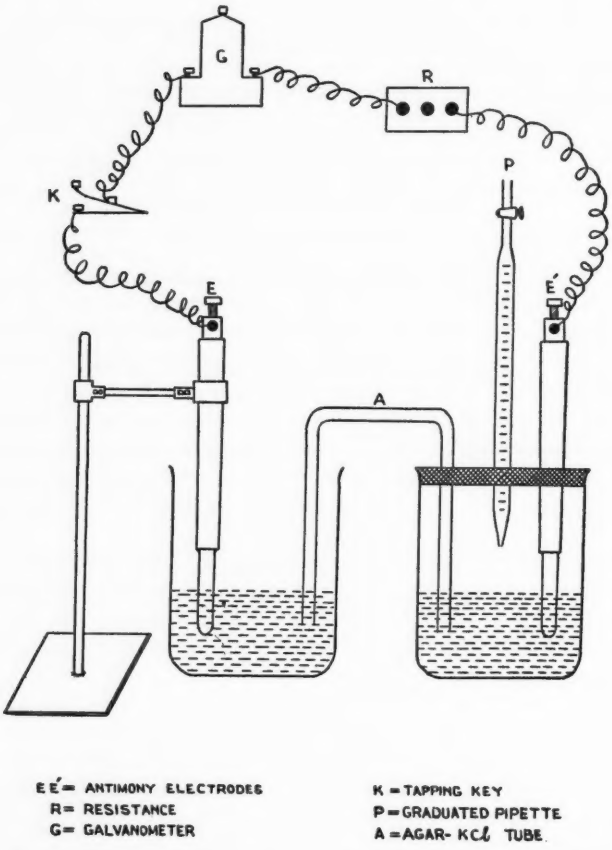

FIG. 1. ARRANGEMENT OF APPARATUS IN THE ELECTROMETRIC-TITRATION METHOD

should cover the whole of the working pH range, and the reproducibility of the antimony electrode potential throughout this range.

The Universal buffer mixture of Prideaux and Ward[2] was chosen for this purpose. It is prepared as follows:

Mix together weighed quantities of the following substances and make up to a liter with freshly boiled distilled water.

1. Potassium dihydrogen phosphate KH_2PO_4 = 5.445 gm.
2. Phenyl acetic acid $C_6H_5CH_2COOH$ = 5.443 gm.
3. Boric acid HBO_2H_2O = 2.466 gm.

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The foregoing mixtures can be made in several lots and stored in test tubes or small bottles, well stoppered. The contents of each test tube or bottle only need to be made up to a liter with distilled water when required. The solution keeps well for several weeks. The titration curve of the Universal buffer is given in figure 2.

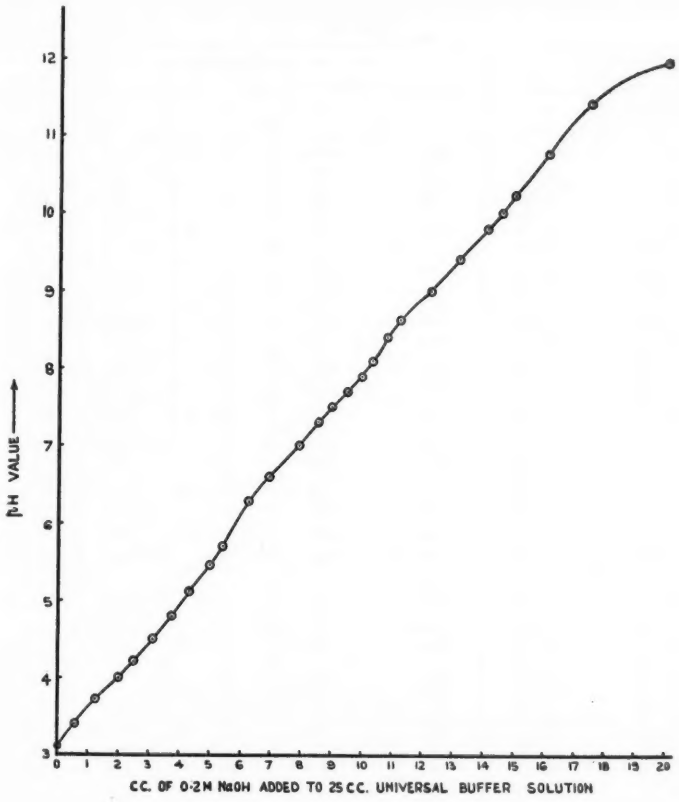

FIG. 2. TITRATION CURVE OF THE UNIVERSAL BUFFER SOLUTION

The electrodes were prepared by melting Merck's pure antimony (Regulus) in a silica dish and pouring it into an iron mould standing vertical and kept heated. The electrodes when cast were about 5 cm. long and about 1 cm. in diameter. They were smoothed and polished on the lathe and soldered on to brass rods having screws at the top for electrical connections. (*See* fig. 1.)

For the successful working of the method it was essential that the uniformity of the behavior of the antimony electrode throughout the pH range of the Uni-

versal buffer should be tested rigorously. The main item of work in this investigation, therefore, centered round this problem; and the results are important not only from the point of view of this method, but equally so in illustrating the behavior of the antimony electrode in general.

TABLE 1

Relation between pH and E.M.F. of antimony electrode (KCl – HCl buffer of pH 2.03 used as standard)

cc. of 0.2 *M* NaOH added to 25 cc. universal buffer and volume made to 50 cc.	pH	E.M.F. milli-volts				
		1	2	3	4	Average
		m.v.	m.v.	m.v.	m.v.	m.v.
0	3.10	54	53	54	53	53.5
0.57	3.40	68	67	68	65	67
1.25	3.73	87	88	93	89	89.25
2.00	4.00	98	...	...	...	.....
2.50	4.21	114	115	113	115	114.25
3.10	4.50	129	134	135	135	133.25
3.75	4.80	143	145	146	144	144.50
4.32	5.1	163	167	167	169	166.50
5.00	5.43	198	200	198	198	198.50
5.40	5.70	226	224	224	228	225.50
6.25	6.30	258	257	257	260	258
6.95	6.60	268	269	266	266	267.25
7.90	7.00	287	282	282	287	184.50
8.55	7.30	...	295	292	297	294.67
9.00	7.50	318	312	308	312	312.50
9.50	7.70	336	326	326	327	328.75
10.00	7.91	348	343	342	344	344.25
10.35	8.10	366	...	...	...	.....
10.85	8.40	373	367	368	365	368.25
11.25	8.62	379	378	373	378	377
12.25	9.00	392	386	395	386	389.75
13.20	9.40	412	411	415	410	412
14.10	9.80	433	429	434	429	431.25
14.55	10.00	456	452	452	453	453.25
15.00	10.21	474	466	465	469	468.5
16.10	10.75	500	495	500	497	498
17.50	11.41	538	529	532	528	531.75
20.00	11.94	566	560	562	559	561.75

RELATION BETWEEN pH AND E.M.F. OF THE ANTIMONY ELECTRODE, USING ANTIMONY ELECTRODE IN KCl – HCl BUFFER OF pH 2.03 AS THE STANDARD

A series of buffer solutions ranging from pH 3.1 to 11.94 were prepared from the Universal buffer solution by taking 25 cc. of the latter, adding the required amount of 0.2 *M* NaOH and making up to 50 cc. The pH values of the buffer solutions were interpolated from a large scale drawing of the titration curve of

the Universal buffer. KCl-HCl buffer of pH 2.03 is easily prepared by mixing 900 cc. of 0.1 *N* KCl with 100 cc. of 0.1 *N* HCl. An antimony rod dipped in this buffer gives an easily reproducible standard electrode in place of the usual calomel half cell.

TABLE 2

Titration of 25 cc. of Universal buffer against 0.2 M NaOH (Sb in KCl — HCl buffer as standard)

NaOH added	E.M.F.				
	1	2	3	4	5
cc.	m.v.	m.v.	mv.	mv.	mv.
0	51	49	47	51	59
	>28	>29	>30	>30	>31
1	79	78	77	81	90
	>21	>22	>23	>21	>20
2	100	100	100	102	110
	>19	>22	>18	>20	>20
3	119	122	118	122	130
	>26	>24	>23	>20	>20
4	145	146	141	142	150
	>44	>44	>45	>44	>44
5	189	190	186	186	194
	>44	>44	>44	>46	>44
6	233	234	230	232	238
	>24	>23	>24	>20	>22
7	257	257	254	252	260
	>19	>19	>17	>20	>18
8	276	276	271	272	278
	>17	>17	>16	>17	>19
9	293	293	287	289	297
	>27	>27	>31	>33	>33
10	320	320	318	322	330
	>30	>28	>31	>27	>27
11	350	348	349	349	357
	>22	>23	>20	>22	>22
12	372	371	369	371	379
	>22	>19	>19	>18	>18
13	394	390	388	389	397
	>25	>25	>26	>23	>23
14	416	415	414	412	420
	>41	>31	>30	>33	>23
15	441	446	444	445	453
	>31	>36	>36	>43	>43
16	482	482	480	488	496
	>22	>31	>31	>28	>28
17	513	513	511	516	524
	>15	>21	>23	>17	>17
18	535	534	534	533	541
	>15	>16	>14	>18	>18
19	550	550	548	551	559
	> 9	> 7	> 8	> 4	> 4
20	559	557	556	555	563

Measurements of E.M.F. were taken with a Crompton box-type potentiometer using a sensitive mirror galvanometer to find the zero position. Four sets of observations were taken at different times. The results given in table 1 show that the greatest variation is not more than 10 m.v. for the same pH in different observations, corresponding to an average difference of about 0.1 pH.

The electrode was cleaned after every observation. The object of this cleaning is to remove the very thin layer of the oxide that is formed when the rod is dipped in a solution.

In order to determine whether the changes in the E.M.F. of an antimony electrode consequent upon the gradual addition of alkali to the Universal buffer

TABLE 3

Titration of 25 cc. of Universal buffer against 0.2 M NaOH (quinhydrone in KCl – HCl buffer as standard)

NaOH added	E.M.F.				
	1	2	3	4	5
cc.	*m.v.*	*m.v.*	*m.v.*	*m.v.*	*m.v.*
0	500	498	500	490	500
	>30	>30	>28	>29	>29
1	530	528	528	519	529
	>20	>19	>19	>22	>20
2	550	547	547	541	549
	>20	>20	>19	>19	>19
3	570	567	566	560	568
	>26	>22	>24	>27	>28
4	596	589	590	587	596
	>42	>46	>45	>43	>49
5	638	635	635	630	645
	>43	>41	>38	>38	>39
6	681	676	673	668	684
	>23	>15	>15	>15	>15
7	704	691	688	683	709
	>17	>19	>19	>21	>18
8	721	710	707	704	727
	>19	>19	>21	>24	>19
9	740	729	728	728	746
	>30	>29	>30	>34	>32
10	770	758	758	762	778
	>27	>28	>27	>22	>28
11	797	786	785	784	806
	>20	>20	>20	>15	>18
12	817	806	805	799	824
	>18	>20	>20	>27	>18
13	835	826	825	826	842
	>23	>24	>24	>22	>24
14	858	850	849	848	866
	>32	>35	>36	>44	>44
15	890	885	885	892	910
	>41	>32	>37	>32	>36
16	931	917	922	924	946
	>29	>21	>18	>24	>19
17	960	938	940	948	965
	>20	>12	>14	>20	>20
18	980	950	954	968	985
	>15	>14	>14	>12	>12
19	995	972	968	980	997
	>13		> 8	>10	>13
20	1,008	.....	976	990	1,010

solution could be reproduced, 25 cc. of the latter were titrated against 0.2 *M* NaOH. In table 2 are given the various sets of values for the E.M.F. corresponding to successive additions of alkali.

Table 2 shows that titrations done at different times are reasonably reproducible. It is also seen that any change in the initial value of E.M.F. between KCl-HCl and Universal buffer is reflected in the subsequent readings so that the successive increments in the E.M.F., for every addition of 1 cc. of 0.2 *M* alkali, are practically constant in the different titrations. These are also included in table 2.

TABLE 4

Titration of 25 cc. of Universal buffer against 0.2 M NaOH (antimony electrode in Universal buffer of pH 3.1 as standard)

NaOH added	E.M.F.		
	1	2	3
cc.	*m.v.*	*m.v.*	*m.v.*
0	6	0	0
	>28	>28	>28
1	34	28	28
	>20	>21	>21
2	54	49	49
	>22	>19	>19
3	72	68	68
	>24	>24	>24
4	96	92	92
	>42	>48	>48
5	138	140	140
	>40		>38
6	178	.....	178
	>18		>18
7	196	.....	196
	>18		>18
8	214	.....	214
	>21		>21
9	235	.....	235
	>28		>28
10	263	.....	263
	>29		>27
11	292	.....	290
	>21		>22
12	313	.....	312
	>19		>18
13	332	.....	330
	>23		>24
14	355	.....	354
	>40		>40
15	395	.....	394
	>36		>36
16	431	.....	430
	>22		>20
17	453	.....	450
	>16		>20
18	469	.....	470
	>13		> 8
19	482	.....	478
	> 7		> 6
20	489	.....	484

QUINHYDRONE STANDARD ELECTRODE

Quinhydrone electrode in KCl-HCl buffer has been successfully used as a standard by several workers. This electrode was also employed in the titra-

tion of the Universal buffer in conjunction with the antimony electrode. The results given in table 3 show slightly greater variations than in the case of standard antimony electrode in KCl-HCl buffer (c.f. table 2). However the successive increments of E.M.F. on the addition of alkali, again show a satisfactory agreement.

Since the basic material in all these titrations is the Universal buffer, it seemed logical to use this very solution as the standard for reference; and thus simplify matters. The result of such titrations are given in table 4 and show a good agreement.

TABLE 5

Change in E.M.F. on successive additions of 1 cc. of 0.2 M NaOH to 25 cc. Universal buffer

ALKALI ADDITIONS	CHANGE IN E.M.F. ANTIMONY IN KCl–HCl	MEAN VALUE MILLI-VOLTS QUINHYDRONE IN KCl–HCl	ANTIMONY IN UNIVERSAL BUFFER
cc.	*m.v.*		*m.v.*
0–1	30	29	28
1–2	21	20	20
2–3	20	19	19
3–4	22	25	24
4–5	44	45	45
5–6	44	40	39
6–7	22	20	18
7–8	19	18	18
8–9	17	20	21
9–10	30	30	28
10–11	29	28	28
11–12	22	20	22
12–13	19	19	18
13–14	24	24	24
14–15	30	34	40
15–16	40	38	36
16–17	30	22	21
17–18	20	17	18
18–19	16	14	11
19–20	7	10	6

It was also found that readings with the Universal buffer as standard were much more satisfactory than with quinhydrone or antimony electrode in KCl-HCl buffer. However, the corresponding increments of E.M.F. on the successive additions of NaOH to the Universal buffer are practically the same in the various sets of observations. This is illustrated in table 5, which records the mean of all increments on the successive additions of alkali in the different sets of observations.

pH VALUE OF SOILS

The electrometric titration method would commend itself for soil work on account of its simplicity and cheapness. The following is a detailed description of the method.

Buffer solutions are prepared by adding 5, 10, 15, and 20 cc. of 0.2 *M* NaOH to 25 cc. of the Universal buffer. These are used to locate the pH range within which the unknown soil suspension may lie. One antimony electrode is dipped in the soil suspension and the other in the aforementioned buffers one at a time. The suspension and the buffer solution are connected with an agar-KCl bridge, and the two electrodes are joined to a galvanometer through a tapping key and suitable resistances to vary its sensitivity (fig. 1). The direction of the current when the circuit is closed shows whether the soil has a higher or lower pH than the standard. After the buffers between which the true pH value lies have been located, 0.2 *M* NaOH is added to 25 cc. of the Universal buffer in amount equal to that corresponding to the buffer having the lower pH value. The antimony rod is then dipped in it and connected to the one in the soil suspension; 0.2 *M* NaOH is then added slowly through a graduated

TABLE 6

pH values of soils as determined by the potentiometric and electrometric titration methods

SOIL LABORATORY NUMBER	POTENTIOMETRIC METHOD	TITRATION METHOD
	pH	*pH*
P.C. 9	5.46	5.44
P.C. 6	5.48	5.44
P.C. 12	5.84	5.70
P.C. 3	7.40	7.46
P.C. 1	7.80	7.84
P.C. 2	7.96	8.10
P.C. 4	8.10	8.10
P.C. 11	8.20	8.16
P.C. 5	8.45	8.56
P.C. 8	8.19	8.21
P.C. 10	8.76	8.70
P.C. 7	9.75	9.82

dropping pipette held in the stopper of the beaker containing the buffer solution. The solution is shaken with a circular motion after each addition and the galvanometer deflection noted till the zero point is reached. Resistance is kept in at first and taken out toward the end of titration. As only about 5 cc. of alkali is to be added at the most, the titrations can be made very rapidly. When the balance is attained the pH value of the soil suspension is equal to that of the buffer. From the total number of cubic centimeters added the pH value of the buffer is ascertained from the graph (fig. 2). Each determination takes about 5 minutes. A dozen soils were examined. The results given in table 6 show a good agreement between the potentiometer and the titration method.

LIME REQUIREMENTS OF SOILS

The electrometric titrations method is particularly suited for bringing a certain solution to a definite pH value. Lime requirement measurements

which aim at bringing the soil to a known pH value by the addition of lime can be carried out very easily as follows:

A solution of pH 6.5 or 7 or any other desired pH is prepared from the Universal buffer by the addition of an appropriate amount of alkali (*see* fig. 2). One antimony electrode is dipped in this buffer and connected to another in the soil suspension as shown in figure 1. Standard lime or baryta solution is then gradually added to the suspension till the galvanometer shows no deflection. The soil has then attained the desired pH and the lime requirement is calculated from the amount of lime or baryta used for the purpose. In order to determine whether the results are reproducible an acid soil of pH 5.44 was titrated to pH 7 with saturated lime water. Soil in lots of 5, 10, and 15 gm. was taken and required 1.7, 3.7, and 5.3 cc. of lime water respectively. It is not intended to discuss the merits of lime requirement methods, but it might be pointed out that the electrometric titration method is independent of the quantity of soil used. It is well known that a number of methods give different results when the quantity of soil is changed.

SUMMARY

A simple electrometric titration method of determining pH value and lime requirement of soil is described.

It makes use of two antimony electrodes, one dipped in the soil suspension and the other in a Universal buffer solution, the pH value of which is continuously varied till a galvanometer through which the two electrodes are joined together shows no deflection. The whole operation of finding pH values is thus reduced to a simple titration.

Lime requirement methods that aim at bringing the soil to a definite pH value can be carried out easily by the technique described in the paper.

A NEW APPARATUS FOR MEASURING SOIL SHRINKAGE

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Soil shrinkage is an important factor in the behaviour of agricultural soils. The appearance of cracks and their consequent injury to the root system of plants are intimately related to this property of soil colloids.

Haines[1] in his study of the volume change associated with variations of water content in soil has described a method of volume measurement by displacement of mercury in a constant-volume bottle. "This bottle has a ground in perforated stopper like an ordinary specific gravity bottle, and the bottom is closed by a glass disc held by a washer and a brass screw-on cap exactly like the end of a polarimeter tube. The removal of this disc allowed the insertion or withdrawal of the soil prism." The technique consisted simply in weighing the mercury required to fill the bottle with and without the soil prism and calculating the displaced volume.

The present investigation was originally undertaken to study the effect of replaceable ions on soil shrinkage. However, it appeared in the early stages of the work that Haines' constant-volume bottle presented certain difficulties which required very careful manipulation to overcome. The temperature changes due to unavoidable handling can be remedied by having a double wall like that in Dewar flasks, but mercury is apt to get into the brass threads and can prove very troublesome. The apparatus described as follows was found to be very satisfactory for such studies and might prove useful to other workers.

DESCRIPTION OF THE APPARATUS

The apparatus shown diagramatically in figure 1 consists of a U-tube with limbs of unequal diameter (31 mm. and 13 mm.). The narrower limb extends to a 100-cc. burette tube attached to it with rubber tubing. It has also a side tube connected to two water reservoirs through pinch cocks, so that the water level in the burette tube can be raised or lowered by opening the upper or lower pinch cock. The U-tube is filled with pure clean mercury, and water is admitted through the side tube until the burette is filled to the top division.

The wider limb of the U-tube has a thick brass cap (also shown separately on a larger scale in the diagram) that fits evenly and has a hole on one side through which passes a thin steel rod ending in a prong. Attached to the

[1] Haines, W. B. 1923. The volume-change associated with variations of water content in soils. *Jour. Agr. Sci.* 13: 296–310.

steel rod is a fine pointed needle. The steel rod can be raised or lowered and clamped in position by the help of a thumb screw. The needle point is viewed through a reading microscope and its point of contact with the mercury surface can be gauged very accurately, as the needle and its shadow can be focussed simultaneously.

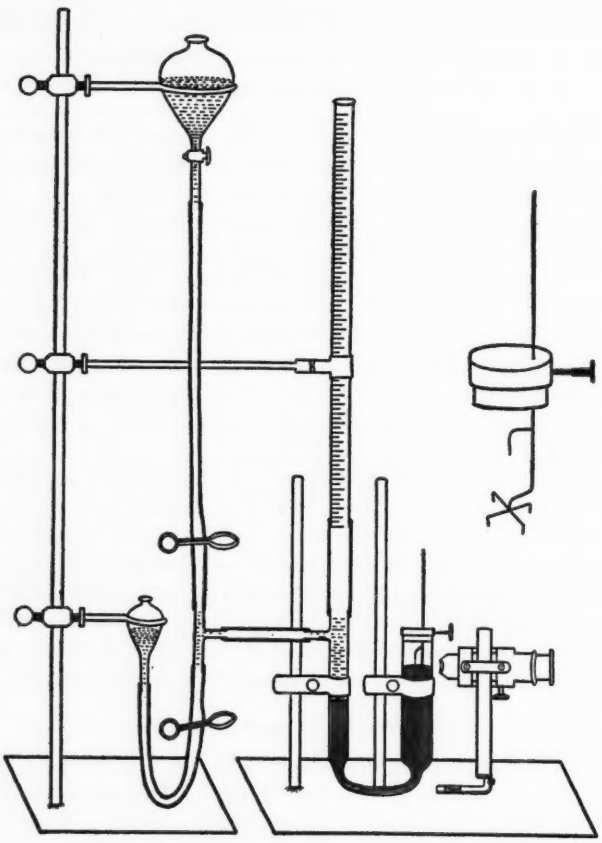

FIG. 1. DIAGRAM OF SHRINKAGE MEASURING APPARATUS
Inset: Brass cap for the wider limb of the U-tube

The zero reading of the apparatus is taken when the needle point just touches the mercury surface and the water level in the burette tube stands near the top. The brass cap is then taken off and soil in the form of a ball is placed on the mercury surface and pushed down with the prong of the steel rod when the cap is replaced in the same position. As a result of the added soil volume, the mercury surface rises. The water level in the burette tube is then gradually

brought down, by opening the lower pinch cock, till the contact is again just made. The fall in the water level is then proportional to the volume of the soil ball, and once the apparatus is calibrated the readings can be taken in a very short time.

Calibration of the instrument is carried out by adding a known weight of mercury to the U-tube, after taking the zero reading, and noting the change in the level of the water level produced thereby. The desired magnification is produced firstly because the density of mercury is higher than that of water, and secondly because the diameter of the limb attached to the burette tube is smaller than the other. To produce a certain change in the level of mercury in the wider limb the level of mercury in the other limb has to be raised or lowered by an amount proportional to the square of the radii of the two limbs.

As the magnification of the instrument can be varied by changing the ratio of the diameters of the two limbs of the U-tube, its sensitivity can be altered to suit individual requirements. In our instrument a magnification of 213 times was attained, so that a change of level of mercury equal to 1 mm. was shown as 21.3 cm. in the burette tube. It might be mentioned that a change in temperature of 5°C. produces a change of less than 0.1 per cent in the magnification due to the alteration in the density of mercury. The calibration, therefore, can be taken to be independent of temperature.

An apparatus of high sensitivity can have only a short total range, for it is not convenient to have a burette tube longer than 100 cm., and consequently it is not possible to measure volumes larger than 3 to 4 cc. For shrinkage experiments this is a decided disadvantage, as volume changes are comparatively small when the total volume has to be kept within 3 to 4 cc. This defect is remedied by taking the zero reading with a glass ball of pre-determined volume (4 to 5 cc.). This volume is added to the soil volume when readings with the latter are taken. The total volume changes due to shrinkage are then comparatively greater, since the soil volume is larger.

EXPERIMENTAL

A 30 to 40-gm. portion of air-dry soil, passing through a 1-mm. mesh sieve, is worked into a paste that just does not stick to the hand, a rubber bung at the end of a glass rod being used to break the crumbs and to get it into a uniform plastic condition. It is then shaped into a ball of convenient size. For this purpose a brass disc with a hole is used as a gauge and the ball is made of a size that just slips through. This is essential when working with a number of soils at the same time in order to keep the readings with the different soils within a narrow range of the instrument.

The soil is worked into a ball, for not only is this shape more convenient to handle but it shows the least tendency to crack on drying. The ball is left in the air for a little while until it is firm enough to be handled without breaking. Its weight is then determined by putting it first into a squat weighing bottle. The weighed soil ball is pushed under mercury in the U-tube and its volume

determined. It is then kept over concentrated sulfuric acid for 2 to 3 hours, after which it is weighed and its volume determined again. In this way a number of readings of weight and volume are taken. The next to the last reading is taken by keeping the soil ball in a vacuum desiccator for 24 hours. The final reading may be taken after the soil has been dried at 100–105°C. in a hot air oven, but it is best to avoid heating.

The results of shrinkage measurements on four soils are shown graphically in figure 2. These have been chosen from a number of soils with a view to

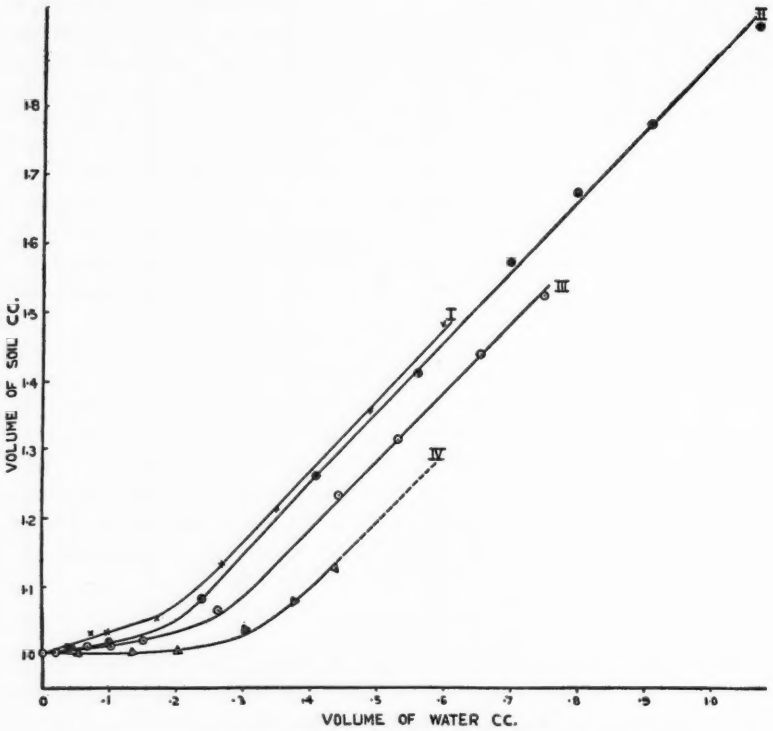

FIG. 2. TYPICAL SHRINKAGE CURVES OF SOILS

convenience of plotting on one scale. The curves are similar to those obtained by Haines, being made up of two portions. The first, or upper, portion of the curve will depend upon the capacity of the soil to imbibe water, and is very short, or even absent, in sandy soils and may be very long in clays. The second, or the lower, portion of the curve depends upon the pore space, since it represents the amount of water lost when the particles have acquired the closest packing. It will be seen that in some soils there is a certain amount of shrinkage along this portion of the curve. Haines has called it "residual shrinkage"

and ascribed it to the films of colloidal material round the solid particles which form small pads between the particles when the first stage of shrinkage has brought them into contact.

The importance of exchangeable bases in modifying physico-chemical properties of soils is well known. An attempt was made to study shrinkage curves of soils saturated with Na, K, Ca, and Ba, in order to determine whether they showed characteristic differences depending upon the nature of the exchangeable bases in them. Soils for this purpose were prepared by leaching with neutral salts, as well as by treatment with hydroxides after removal of the original bases by leaching with 0.05 *N* HCl. The results showed no characteristic differences due to various ions, so that whatever effect the exchangeable ions might have in modifying other physical properties of soils, they have no appreciable influence on shrinkage.

SUMMARY

A new apparatus for measuring pore space, apparent density, and shrinkage of moist soil on drying is described.

Typical shrinkage curves of a few soils are given.

The nature of exchangeable ions in soil has no appreciable influence on the character of its shrinkage curve.

OXIDATION REDUCTION POTENTIALS IN SOILS: I. PRINCIPLES AND ELECTROMETRIC DETERMINATION[1]

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Oxidation reduction potentials of biological systems have been studied by a continuously increasing number of investigators since the suggestive data procured by Gillespie (8) was published in 1920. Warburg (19) has demonstrated the essential character of iron in biological oxidations and Michaelis and Smythe (15) have shown that many iron compounds present in biological systems have definite oxidation reduction potentials. Hopkins (12) pointed out the importance of glutathione in certain biological systems, and Lund (14) showed that it has a stable oxidation reduction potential. The actions of numerous other compounds important in biological oxidations have been shown to be accurately accounted for by their oxidation reduction potentials.

Willis (21) found that liming certain soils to pH 6.2 caused a chlorotic condition of the plants due to the soil manganese becoming unavailable. This can not be explained on the basis of reaction alone, but, as Willis points out, is explainable when the Eh[3] as well as pH of the soil is considered.

The important findings in the field of bacteriology and biochemistry made possible by use of oxidation reduction potentials have made it desirable to obtain more data concerning these potentials in soils. By the use of such data it may be possible to determine the more exact nature of certain soil processes and phenomena which may be important in plant growth. Many phases of the soil- soil microörganism and plant balance in nature may be further explained by the application of similar data in the future.

A search through the literature revealed no rapid, accurate method of determining the oxidation reduction potential of soils while they were in a condition similar to that existing in the field.

This paper reports a comparison of over 50 methods and the proposal of a rapid procedure of sufficient accuracy for comparative tests.

[1] Experimental work reported in this paper was performed in the agronomy laboratories with aid of equipment lent by the department of agricultural and biological chemistry at Pennsylvania State College, State College, Pa.

The author is indebted to Dr. F. G. Merkle, associate professor of soil technology, agronomy department, and Dr. M. W. Lisse, professor of biophysical chemistry, department of agriculture and biological chemistry, for their invaluable aid in preparation of this paper.

[2] Graduate assistant in soil technology.

[3] Eh and oxidation reduction potential are used synonomously in this paper.

The theoretical development of the expression that equilibrates an oxidation reduction potential and the system it represents is given in many theoretical chemistry books (3, 7, 9) and in the excellent works of Clark (4) and Hewitt (11). It will be necessary, however, to repeat a few facts stated in these references in order to make it clear to the soil scientist that this rather new phase of soil study has a precise theoretical foundation.

Beginning with the definition that oxidation is the loss of electrons and reduction is the gain of electrons, Hewitt (11) derives the relation.

$$\text{Eh} = \text{Eo} - \frac{RT}{nF} ln \frac{(\text{Ox.})}{(\text{Red.})}$$

where Eh = the potential in volts, referred to the normal hydrogen electrode as zero, of the system under consideration
Eo = a constant characteristic of the system
R = gas constant = 8.3107 volt coulombs
T = absolute temperature
F = Faraday = 96,500 coulombs
n = number of electrons involved in the change from the oxidized to reduced form
ln = natural logarithm
(Ox.) = Concentration of oxidized form
(Red.) = Concentration of reduced form.

Since R and F are constant, T may be kept constant, n assumed equal to 2, and changing to common logarithms the equation becomes:

$$\text{Eh} = \text{Eo} - 0.03 \log \frac{(\text{Ox.})}{(\text{Red.})} \text{ at } 30°\text{C.}$$

The equation shows Eh to be dependent on the ratio of oxidant to reductant as well as on temperature and the particular system under consideration. Also the system must be reversible, i.e., the oxidized form readily changing to the reduced form under the influence of suitable Eh and the reduced form readily changing to the oxidized form. In biological systems the reversibility and proportions of different substances are never fully known. Conant (5), however, points out that even if some compounds present are irreversible, there will be a certain equilibrium present which is accurately described by the oxidation reduction potential revealed by the entire system.

ANALOGY TO pH

In describing action or energy, two factors or measurements of the change may be considered; first, quantity factor; and second, intensity factor. The term Eh relates strictly to intensity and gives no measure of the capacity of the system for oxidation reduction processes.

The following shows the likeness of acidity or basicity to oxidation reduction:

	ACIDITY OR BASICITY	OXIDATION REDUCTION
Measure of quantity factor	Titration	Measure of CO_2 evolved
Measure of intensity factor	pH	Eh
Term applied to resistance to change of intensity factor	Buffer capacity	Poise

METHODS OF MEASURING OXIDATION REDUCTION POTENTIALS

Methods of measuring Eh, like those of measuring pH, are of two types; colorimetric, and electrometric.

The dependability of colorimetric methods is not agreed upon. Thornton (18) obtains good results with methylene blue in milk systems, as do Needham and Needham (16) with various indicators in cells. Clark (4) however, reports that methylene blue, a favorite for this type of study, does not react as a reliable reduction indicator. Many European investigators have used indicators in biochemical research, but apparently they are not as reliable for measuring Eh as the indicators used in pH work are for their purpose.

Electrometric methods of measuring Eh show more promise of providing a precise measurement of oxidation reduction intensities than do colorimetric methods. The electrometric method consists of building an electric cell in which the system to be tested is one half and the other half is usually a calomel cell. The unknown half cell consists of an unattackable electrode immersed in the system to be tested. The electrode is connected to the potentiometer and the test solution connected to the calomel cell by means of an electrolyte bridge.

The dependability of numerous types of electrodes for measuring Eh has been tested (2, 4, 6). The common conclusion of these tests is that bright platinum is the most suitable electrode.

Clark and Cohen (4) use a Leeds and Northrup type K potentiometer and a Leeds and Northrup Type R galvanometer for measuring Eh. Hewitt (11) prefers a Lindemann galvanometer with which he notices no errors due to polarization in weakly poised biological systems. Allyn and Baldwin (1) find a vacuum tube potentiometer gives the most sensitive results with bacterial suspensions.

ELECTROMETRIC METHODS USED IN SOILS

Gillespie (8) measured oxidation reduction potentials of water-logged soils by allowing platinum electrodes to remain in the soil covered with water and measuring the potential each day. The small part of the soil contaminated by the KCl bridge was discarded after each measurement.

Remesow (17) prepared soil suspensions and after allowing them to set for

15 to 18 hours, inserted three electrodes into each and allowed them to stand over night. He then measured the potential at each electrode.

Herzner (10) compared numerous methods of measuring the Eh of soils. He obtained the best results with the soil placed in a Gooch crucible and set in a pan containing a shallow depth of boiled distilled water. When the water appeared at the surface of the soil an electrode of a bright platinum coil of wire sealed in a glass tube was placed in the soil and the potential determined within an hour.

Willis (20) shakes the suspension of soil and water for 3 days in an open flask. Then he transfers the soil suspension to a special electrode flask. The oxygen of the suspension is replaced by purified nitrogen while the system is under reduced pressure. The potential of the oxygen-free soil is then measured.

EXPERIMENTAL

The object of the experimental procedure was to find the most accurate method, as indicated by likeness of replicates, that included the following desirable features.

1. Soil as near as possible to the condition it exists in the field. In this connection the treatment of the soil must be such that anaerobic bacteria do not have time to become very active. Also the ratio of soil to water must be as narrow as possible and still insure good contact with the electrode.
2. Determinations must consume as little of the analyst's time as possible.
3. Cost of equipment must be small.

Preparation of electrodes. Herzner (10) and Clark (4) found that slight variations in electrodes may not show differences in the potential of highly poised oxidation reduction systems, but may cause decided differences in slightly poised systems like soil or bacterial suspensions. With this in mind electrodes were made of 3½-inch lengths of 22 B & S gauge platinum wire. One-eighth of an inch of the wire was fused to a 6-inch length of 18 B & S gauge copper wire. The copper wire was drawn through a 4½-inch length of small bore glass tubing and sealed into position as shown in figure 1.

The hook of copper wire was placed in a small well of mercury to make contact with a wire to the potentiometer when the potential of the electrode was being measured.

Twelve electrodes showed the same potential within 0.5 millevolt for a 0.01 *M* potassium ferrocyanide, 0.001 *M* potassium ferricyanide, and 2 *M* KCl solution.

Soils used. Hagerstown clay loam surface, Dekalb loam surface, and Moshannon clay loam surface soils were used. They all gave about the same variation for a single method, and only the results for the Moshannon soil are here reported. The soils had all been stored in bins in the air-dry condition for from 1 to 2 years when the potentials were determined.

Potentiometer and galvanometer. A Leeds and Northrup type K potentiometer and a Leeds and Northrup enclosed lamp and scale galvanometer were used. The galvanometer has a sensitivity of 40 megohms, a coil resistance of

970 ohms, an external critical damping resistance of 17,000 ohms, and a period of 3.2 seconds. Although a more sensitive galvanometer probably could be used to advantage, no polarization effects were noticed after the first potential for each soil was read, and only occasionally did these effects bother in the first reading. A very quick light tap of the contact key to the galvanometer was practiced in order to guard against polarization. A saturated calomel cell was used as a reference electrode.

Procedures. In most of the methods or procedures vials of 30-cc. capacity and 3 inches long were used as containers for the soil suspensions. In one group of methods, however, it was necessary to use Gooch crucibles to hold the soil and water mixture. All trials were made in quadruplicate. The deviation of the mean was calculated by Bessel's formula (13) for experimental error and used as an indication of the likeness of the four values obtained for a certain method and soil.

The first group of trials was designed to show the effect of increasing lengths of time that soil, water, and electrodes were in contact with one another. In this study a soil to water ratio of 1 to 1 was used. The soil and water were thoroughly pestled together before the electrodes were inserted, and the soil suspension was stirred with the electrode just prior to measuring the potential. Table 1 shows the results of this first study.

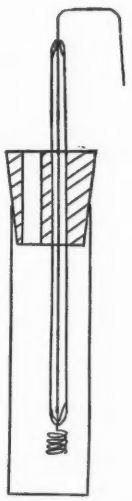

FIG. 1. TYPE OF HALF CELL USED

Table 1 shows that 12 hours or more of water-logging causes a decided negative shift in the potential of a soil. Soil and water contact of very short or very long periods apparently produces potentials that are very variable. The results in table 1 indicate that the method of Remesow (17), which involves water-logging for at least 24 hours, allows considerable opportunity for a negative shift in potential.

The second set of procedures compared the one recommended by Herzner (10) with modifications of this method. In these tests contact between the soil suspension and electrode was assured by tapping the Gooch crucible and contents on a rubber stopper several times. Methods 10 to 14 in table 2 give the results obtained in this group of tests.

Numbers 10 and 12 showed a low enough deviation of the mean to be promising procedures. However, number 10 shows such a high Eh mean, probably due to placing the electrode in the dry soil, that it was discarded in favor of other methods that gave as uniform results of a lower mean value. Number 10 and especially number 12 showed much less dependable results with other soils than with the Moshannon soil. All of these methods were finally discarded as being less reliable and a little more difficult to manipulate than ones studied later.

The trials numbered 15 to 23 in table 2 were designed to test the effect of

short-time treatment of the soil suspension with purified nitrogen gas. The very large deviation of the mean with all variations tried shows that a strenuous manipulation of the soil is probably necessary to remove the oxygen uniformly from the soil suspension. The quantitative removal of oxygen from the soil suspension is assumed to be unnecessary and perhaps undesirable, as it creates a condition in the soil quite different from that in the field.

Methods numbered 24 to 29 in table 2 give results obtained when the soil suspension was treated with heat, reduced pressure, and centrifuging.

Numbers 25 and 26 gave much larger deviations of the mean with other soils than with the Moshannon soil. Number 29 was selected for further study and the others were discarded as giving results too variable.

Further studies were decided upon from the results shown in tables 1 and 2, and similar data on other soils. Methods 3, 4, 5, and 29 were selected as more likely to lead to a satisfactory procedure.

TABLE 1

Effect of varying lengths of time soil, water, and electrode were in contact

Results obtained with Moshannon soil, pH value 5.8

METHOD NUMBER	TIME OF CONTACT	Eh MEAN	DEVIATION OF MEAN
		volts	*volts*
1	10 min.	+0.529	±0.008
2	30 min.	+0.528	±0.005
3	1 hr.	+0.520	±0.003
4	2 hr.	+0.530	±0.002
5	4 hr.	+0.518	±0.003
6	6 hr.	+0.480	±0.009
7	12 hr.	+0.436	±0.005
8	116 hr.	−0.040	±0.005
9	240 hr.	−0.146	±0.014

The effect of soil to water ratio, time (within rather narrow limits) of soil water and electrode contact, time of centrifuging, pestling soil and water together before inserting electrode, and stirring with electrode just before measuring the Eh were studied. Table 3 shows the results of these studies.

Trial 30 was on a bin sample taken at a date previous to the thoroughly homogenized sample used for all other methods shown in table 3.

Procedures 31 to 36 show that similar results will be obtained if the time of electrode, water, and soil contact is between 1 and 5 hours. They also show that nothing is gained by stirring the suspension with the electrode just prior to making the potential measurements.

Methods 37 to 42 show that soil to water ratios ranging from 7 gm. of soil and 7 cc. of water to 7 gm. of soil and 4 cc. of water give a closer agreement of replicates than ratios in which less water was used in this soil (a clay loam). Numbers 37 to 48 show that a soil, water, and electrode contact of 35 minutes

TABLE 2

The results of various methods of determining the Eh value of the Moshannon soil

pH value 5.8

METHOD NUMBER	SOIL TO WATER RATIO*	TIME OF CONTACT†	TREATMENT	Eh MEAN	DEVIATION OF MEAN
				volts	*volts*
10	Maximum water capacity	90 min.	Electrode and dry soil in Gooch crucible, water from below, and Eh measured after 1½ hours	+0.556	±0.002
11	Maximum water capacity	15 min.	Soil in Gooch crucible, water from below electrode in soil 15 minutes prior to Eh reading	+0.516	±0.005
12	Maximum water capacity	60 min.	Soil in Gooch crucible, water from below and stand one hour, then electrode in soil 1 hour	+0.491	±0.001
13	Maximum water capacity	2 hr.	Soil in Gooch crucible, water from below, and stand one hour, then electrode in soil 2 hours	+0.515	±0.004
14	Maximum water capacity	15 hr.	Soil in Gooch crucible, water from below and stand one hour, then electrode in soil 15 hours	+0.395	±0.010
15	7:7	140 min.	Electrode, soil and water in contact 1 hour under reduced‡ pressure. Released with N_2 stirred, pressure reduced for 1 hour again and released with N_2	+0.378	±0.019
16	7:7	120 min.	N_2 bubbled through suspension for 10 minutes just before Eh was measured	+0.436	±0.023
17	7:7	135 min.	N_2 bubbled through suspension for 15 minutes just before Eh was measured	+0.491	±0.010
18	7:7	15 min.	N_2 bubbled through suspension for 15 minutes	+0.484	±0.012
19	7:7	13 hr.	Na_2 bubbled through suspension for 10 minutes just before Eh was measured	+0.354	±0.015
20	7:7	15 hr.	Soil, water and electrode in contact under reduced pressure. Released with N_2	+0.296	±0.027
21	7:7	90 min.	Stirred thoroughly with a stream of N_2 before electrode was inserted and just before Eh was read	+0.455	±0.017
22	7:7	3 hr.	Stirred with N_2 stream before and during Eh measurement	+0.498	±0.008
23	7:7	20½ hr.	Stirred thoroughly with stream of N before electrode was inserted	+0.362	±0.012
24	7:7	2 hr.	Reduced pressure 1 hour, released, suspensions stirred, reduced pressure 1 hour again, released stirred and Eh determined	+0.450	±0.008

* First figure is soil in grams, second figure water in cubic centimeters.

† Soil, water, and electrode contact.

‡ Reduced pressure in all cases was about 4 cm. of mercury.

TABLE 2—*Concluded*

METHOD NUMBER	SOIL TO WATER RATIO*	TIME OF CONTACT†	TREATMENT	Eh MEAN	DEVIATION OF MEAN
				volts	*volts*
25	7:7	70 min.	Heated to 90°C., pressure reduced for 40 minutes, released, cooled for 25 minutes, stirred and Eh read	+0.430	±0.004
26	7:7	3 hr. 15 min.	Reduced pressure 3 hours, released, stirred and Eh determined	+0.515	±0.003
27	7:7	14 hr.	Reduced pressure 14 hours, released, stirred and Eh determined	+0.351	±0.021
28	7:7	30 min.	Reduced pressure 20 minutes, released, stirred and Eh determined	+0.513	±0.010
29	7:7	35 min.	Centrifuged for 5 minutes just prior to Eh measurement	+0.466	±0.002

TABLE 3

Effect of soil: water ratio, centrifuging and other variations on stability of Eh measurement

Results with Moshannon soil, pH value 5.8

METHOD NUMBER	SOIL: WATER RATIO*	TOTAL TIME SOIL, ELECTRODE, AND WATER WERE IN CONTACT	TIME CENTRIFUGED	SOIL AND WATER PESTLED AT START	STIRRED WITH ELECTRODE JUST BEFORE MEASURING	VIAL AND CONTENTS TAPPED TO MAKE CONTACT WITH ELECTRODE	Eh MEAN	DEVIATION OF MEAN
							volts	*volts*
30	5:3	2 hr.	.....	Yes	Yes	No	+0.515	±0.003
31	7:4	75 min.	.....	Yes	Yes	No	+0.461	±0.002
32	7:4	2 hr. 40 min.	.....	Yes	Yes	No	+0.457	±0.003
33	7:4	4 hr. 50 min.	.....	Yes	Yes	No	+0.458	±0.003
34	7:4	1 hr.	.....	Yes	No	No	+0.455	±0.002
35	7:4	2 hr.	.....	Yes	No	No	+0.463	±0.002
36	7:4	3 hr.	.....	Yes	No	No	+0.460	±0.004
37	7:7	35 min.	5 min.	Yes	No	No	+0.466	±0.002
38	7:5	35 min.	5 min.	Yes	No	No	+0.477	±0.002
39	7:4	35 min.	5 min.	Yes	No	No	+0.465	±0.002
40	7:35	35 min.	5 min.	Yes	No	No	+0.464	±0.007
41	7:32	35 min.	5 min.	Yes	No	No	+0.468	±0.005
42	7:3	35 min.	5 min.	Yes	No	No	+0.481	±0.005
43	7:4	65 min.	5 min.	Yes	No	No	+0.445	±0.001
44	7:4	15 min.	5 min.	Yes	No	No	+0.473	±0.004
45	7:4	45 min.	5 min.	Yes	No	No	+0.473	±0.005
46	7:4	50 min.	10 min.	Yes	No	No	+0.479	±0.005
47	7:4	20 min.	10 min.	Yes	No	No	+0.468	±0.003
48	7:4	125 min.	5 min.	Yes	No	No	+0.468	±0.002
49	7:35	35 min.	10 min.	No	No	Yes	+0.455	±0.006
50	7:32	40 min.	10 min.	No	No	Yes	+0.474	±0.004

* First figure is soil in grams, and second figure is water in cubic centimeters.

TABLE 4

Eh, mean Eh, deviation of mean, and pH of soils of widely varying properties when determined by the method of pestling and centrifuging

SOIL	HORIZON	DEPTH	Eh	MEAN Eh	DEVIATION OF MEAN	pH
		inches	*volts*	*volts*	*volts*	
Hagerstown silt loam (a virgin profile from near State College, Pa. Collected by Dr. F. G. Merkle) A typical Gray Brown Forest Soil	A0*	0–1	+0.524			
	A0	0–1	+0.526			
	A0	0–1	+0.539*			
	A0	0–1	+0.529	+0.530	±0.002	4.41
	A1	1–3	+0.533			
	A1	1–3	+0.516			
	A1	1–3	+0.523			
	A1	1–3	+0.524	+0.524	±0.002	4.89
	A2	3–6	+0.517			
	A2	3–6	+0.513			
	A2	3–6	+0.514			
	A2	3–6	+0.518	+0.516	±0.001	4.92
	B1	6–20	+0.505			
	B1	6–26	+0.518			
	B1	6–20	+0.504			
	B1	6–20	+0.510	+0.509	± 0.002	5.29
	B2	20–48	+0.529			
	B2	20–48	+0.530			
	B2	20–48	+0.525			
	B2	20–48	+0.526	+0.528	±0.001	5.13
Otisville Sandy Loam (A virgin profile from near Equinunk, Pa. Collected by L. A. Brown) A typical podsol	A0*	0–3	+0.565			
	A0	0–3	+0.554			
	A0	0–3	+0.566			
	A0	0–3	+0.562	+0.562	±0.002	3.67
	A1	3–5	+0.628			
	A1	3–5	+0.625			
	A1	3–5	+0.636			
	A1	3–5	+0.628	+0.628	±0.002	3.79
	B1	5–6	+0.489			
	B1	5–6	+0.487			
	B1	5–6	+0.496			
	B1	5–6	+0.504	+0.494	±0.002	3.70
	B2	6–13	+0.507			
	B2	6–13	+0.506			
	B2	6–13	+0.496			
	B2	6–13	+0.490	+0.500	±0.003	4.46

* In these organic layers 3 gm. of material to 10 cc. of water was used to make the test.

TABLE 4—*Concluded*

SOIL	HORIZON	DEPTH	Eh	MEAN Eh	DEVIATION OF MEAN	pH
		inches	*volts*	*volts*	*volts*	
A typical podsol—*Concluded*	B3	13–23	+0.500			
	B3	13–23	+0.509			
	B3	13–23	+0.517			
	B3	13–23	+0.509	+0.509	±0.002	4.82
	C	23–29	+0.489			
	C	23–29	+0.479			
	C	23–29	+0.484			
	C	23–39	+0.484	+0.484	±0.001	5.47
Matanzas Clay (Perdigan phase from Cuba)	Soil	0–6	+0.466			
	Soil	0–6	+0.468			
	Soil	0–6	+0.470			
	Soil	0–6	+0.465	+0.467	±0.001	7.67
	Subsoil	6–20	+0.485			
	Subsoil	6–20	+0.477			
	Subsoil	6–20	+0.481			
	Subsoil	6–20	+0.483	+0.482	±0.001	7.79

is sufficient for accurate results if the mixture is centrifuged for the last 5 minutes of the period of contact.

In view of the results obtained by use of these 50 methods, number 39 has been selected as best combining simplicity, rapidity, and dependability of results. Procedure 39 was further used on 13 soils to test its dependability on soils differing widely with respect to the nature and quantity of colloidal material present. Results of this test are given in table 4.

All horizons of the Hagerstown soil had been stored in the laboratory, air-dry for 2 years; the Otisville had been stored in similar condition for 6 months; and the Matanzas for 2 months. The method used gives comparative Eh values. However, we must look to future studies for an accurate interpretation of oxidation reduction potentials when they are determined on soils of known physical, chemical, and microörganic properties.

DEPENDABILITY OF RESULTS

Bessel's formula, which was used in calculating the deviation of the mean, was further employed to calculate the probable error of the difference of two values. It shows that a difference between means of .010 volt will be a significant difference 40 out of 41 times that two mean values such as those in table 4 are compared.

On the basis of the results reported in table 4 the method used to obtain them is suggested as a reliable, simple method of measuring the oxidation reduction potentials of soils.

DETAILS OF METHOD

The soil is ground with a rubber pestle to break all granules. Solid particles larger than 1 mm. in diameter are sieved out. The sieved sample is thoroughly mixed. For each measurement 7 gm. of soil in a 30-cc. vial is used. To the soil is added 4 cc. of distilled water. More than 4 cc. of water may be necessary for heavy clay soils. The ratio within narrow limits is not important, however (*see* table 3, methods 37 to 42). The soil and water are rubbed into intimate contact with a glass rod.

The electrodes are cleaned just prior to each determination either by immersing in hot strong HNO_3, rinsing with water, then immersing in 2 *N* NH_4OH and rinsing with distilled water; or by immersing in chromic sulfuric acid cleansing solution a few minutes, rinsing in distilled water, and flaming in an alcohol flame. The latter method gives slightly better results. The electrode is placed in the suspension of soil in water within a few minutes after the suspension is prepared. The electrode is held in its rubber stopper in such a manner that the platinum spiral is completely submerged, but does not touch the bottom of the vial (*see* fig. 1).

The soil suspension and electrode are left in contact for 30 minutes. The vial and contents are then placed in a centrifuge (the bottom of the centrifuge cups were padded with cotton to prevent breakage of the vials) and centrifuged at 256 times gravity for 5 minutes. The potential of the suspension is measured as soon as the centrifuge is stopped.

SUMMARY

A few of the principles of oxidation reduction potentials applicable to biological systems are briefly restated from previous publications (4, 11).

A comparison of 70 methods (details of 50 are given) of measuring oxidation reduction potentials revealed a procedure which embodies the following qualities:

Soil very near its condition in the field when potential is measured.
Each determination consumes a comparatively short period of the analyst's time.
Little equipment other than that used in the electrometric measurement of pH is needed.

A method is proposed in which the soil and water mixture is thoroughly pestled, the electrode inserted, and the whole centrifuged in order to insure intimate contact. The Eh is read immediately. Potentials obtained by this method are comparative, and have a deviation of the mean of not more than .003 volt.

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BOOK REVIEW

American Peat Deposits. By A. P. Dachnowski-Stokes and V. Auer. In Handbuch der Moorkunde, VII. Gebr. Borntraeger, Berlin, 1933. Pp. vi + 242, pl. 9, figs. 43.

Recent progress in peat investigations is due in large measure to the problems presented by a desirable utilization of "submarginal" land and by the demand for standard grades of commercial peat products. That a fuller understanding of vertical cross sections and a more detailed description of peat profiles have the broadest application in physical and biochemical studies of organic matter, as well as for practical purposes is now conceded. That greater emphasis should be laid on genetic, historical, and developmental features of peat land for purposes of classification has been realized only recently.

The book just issued is volume VII of a series of 10 books contributed by specialists of different countries, and edited by Dr. K. von Bülow.

Part I of the book deals with peat deposits in the United States and their characteristic profiles and classification, and has been written by Dr. A. P. Dachnowski-Stokes of the U. S. Bureau of Chemistry and Soils. The major groups of peat land are associated with predominating environmental conditions of climate, vegetation, and land relief. The subdivisions have been outlined on the basis of inherent morphological and developmental features of distinctive type profiles and on the degree of decomposition and characteristic properties of peat soils produced in different environments.

Part II presents a general and interpretative contribution on "Peat bogs in southeastern Canada" by Dr. V. Auer of Finland. The use of pollen-analysis technique by the author indicates that changes in forests and presumably in climate correspond to those established in Europe.

Part III is entitled "Die Moore Südamerikas, insbesondere Feuerlands" and is also written by Dr. Auer. The graphical presentation of highmoors in Tierra del Fuego and the significant discussion of the changes in vegetation should make this part particularly helpful to the more technically minded student.

The "America" volume deserves closer consideration by workers in pedology, ecology, and geography, and by those whose interest lies in the agricultural, industrial, and other uses of peat land resources.

A. G. McCall.